

## **MASS SPECTRA AND ISOTOPES**

# MASS SPECTRA AND ISOTOPES

BY

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LONDON  
EDWARD ARNOLD & CO.

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*First Published in 1933*

*Second Edition 1942*

*Reprinted 1944, 1946, 1948*

Printed in Great Britain by  
Butler & Tanner Ltd., Frome and London

## PREFACE TO FIRST EDITION

It is now nine years since the publication of the second edition of *Isotopes* and the large development of the subject has led me to narrow the scope of the book a little. As the change in the title is intended to indicate, it is now concerned less with general theory and more with experimental results, especially with those obtained by mass-spectrum analysis. In Part III I have attempted to give an account of each individual element relative to its isotopic constitution, a nuclear "chemistry" which so far as I am aware is the first of its kind. The rapid development of artificial transmutation of elements appears likely to create a demand for collected data of this kind in an easily accessible form.

For the contribution of the two chapters on the Isotope Effect in Optical Spectra I am indebted to Dr. C. P. Snow who has made this subject a special study. I have every reason to hope that his treatment of the theory will be welcome to all students of this intricate and rapidly widening field of research.

I wish to thank Professor R. H. Fowler for valuable advice and Dr. K. T. Bainbridge for generous help in connection with the inclusion of his latest work. My thanks are also due to Professors R. T. Birge, A. J. Dempster, F. Soddy and H. C. Urey for providing me with illustrations; to the Council of the Royal Society, the Council of the Chemical Society, Messrs. Macmillan & Co. and Messrs. John Murray for the use of certain plates and figures.

F. W. ASTON.

CAMBRIDGE,

July, 1933.

## PREFACE TO SECOND EDITION

It was my original intention that this book should have appeared 10 years ago. It is clearly unnecessary to specify the particular circumstances which caused this delay, and I hope they will be taken into account when the shortcomings of the book are criticized. Since the publication of the First Edition in 1933 in one important sense at least the subject may be said to have been closed. All the elements have now been analysed, and my main concern in writing this book is to tell how this has been done. In consequence I have paid my best attention to Part III, the "nuclear chemistry" mentioned in

## PREFACE

the previous preface. There will be found, with full references, the whole of the evidence upon which the first International Table of Stable Isotopes was drawn up in 1936, and the later work upon which its subsequent annual publications have been based. As chairman of the committee concerned I am in a particularly favourable position to compile this. In this edition, to facilitate reference, the elements are described in their natural order instead of in their chemical groups.

To record the remarkable advances in design of mass spectrographs, particularly the double focusing types, an entirely new Chapter has been added in which a large number of very accurate measurements of mass are tabulated.

I wish to thank Dr. C. P. Snow for revision of the chapters dealing with Optics, and Dr. M. Goldhaber for help in collecting material. I repeat acknowledgments made in the Preface to the First Edition with respect to illustrations, and add to them the names of Professors A. O. Nier and J. Mattauch.

F. W. ASTON.

CAMBRIDGE,

*December, 1941.*

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# MASS SPECTRA AND ISOTOPES

## PART I HISTORICAL CHAPTER I INTRODUCTION

**1. Introduction.**—Towards the end of the last century the attitude of science in relation to the atomic theory started to undergo a complete and radical change. What had been before regarded as a convenient working hypothesis became with remarkable rapidity a definite statement of fact.

This transformation is now complete and in any well-equipped laboratory to-day not only can individual atoms be detected but the movements of the swiftest of them can be tracked and made visible even to the untrained eye.

The causes of this remarkable advance are to be ascribed in particular to the discovery of radioactivity, which has provided us with atomic projectiles possessing enough energy to produce visible and measurable effects individually, and in general to the steady and continuous improvement in technical methods. Subject to such unprecedented scrutiny it was to be expected that the fundamental physical theories which underlie the applied science of chemistry and form a solid mathematical foundation for its formulæ, might show hitherto unsuspected flaws. Such expectations began to be realized when, among the radioactive elements, Boltwood failed to separate ionium from thorium, and, among the inactive elements, when Sir J. J. Thomson a few years later observed the anomalous behaviour of neon when subjected to positive ray analysis. Further and still more delicate and careful scrutiny of these flaws revealed them, as it must always do, if they are real, not as fortuitous and disconnected, but as a definite and ultimately intelligible pattern. It is with the interpretation of this pattern, so revealed, that this volume is con-

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cerned, so that it will be of interest to look back rather over a century to the beginning of the theories which form the background against which it was first observed.

**2. Hypotheses of Dalton and Prout.**—In the generalization, known as the Atomic Theory, put forward by Dalton in 1803, which laid the foundations of the whole of modern chemistry, five postulates were laid down, and it is a striking tribute to the shrewd intuition of that observer that, of those five, to this day, the validity of one only is in any question. This postulate is that : Atoms of the same element are similar to one another and equal in weight. It obviously consists of two parts and if we combine both as a definition of the word element the whole becomes a truism ; this aspect of the matter will be considered later on. For the present we shall take the word "element" to mean what Dalton evidently intended it to mean, and what we generally consider it to mean to-day, namely a substance such as chlorine or lead which has constant chemical properties, and which cannot be resolved into further components by any known chemical process. The first half—taken together with the other four postulates—is then sufficient to define the word "element" and the second becomes a pure hypothesis.

About ten years later Prout suggested that the atoms of the elements were all made up of aggregations of atoms of hydrogen. On this view the weights of all atoms must be expressed as whole numbers, and if, as postulated by Dalton, the atoms of any particular element are all identical in weight, the atomic weights and combining ratios of all elements must be whole numbers also. Chemists soon found that in the case of many elements this was certainly not in agreement with experiment ; the more results they obtained the more impossible it was to express the atomic weights of *all* the elements as whole numbers. They therefore had to decide which hypothesis, Dalton's or Prout's, they would adopt. There was little doubt as to the result of the decision and in due course Prout's theory was abandoned.

It is interesting to consider the reasons which led to a decision which the subsequent history of science proves to have been as wise in principle as it was wrong in fact. The alternative views were—either an element was composed of atoms of identically the same weight, when in certain elements the weights of the individual atoms must be fractional, or these particular elements were composed of atoms of different weights mixed together, so that though the individual weights of the atoms would still be whole numbers their mean would be a fraction. It is almost inconceivable that the second alternative never occurred to philosophers during the time when the

decision hung in the balance—indeed it was far more likely to be considered then than years later when Dalton's view had been generally accepted—but the objections to it were immediate and formidable. The idea that particles could behave in a practically identical manner even though they had different weights is not one that commends itself, *a priori*, to common sense, and as a working hypothesis for chemists it is as hopeless and indefinite as the simpler alternative is distinct and inspiring. Also it could be urged that the objections to the fractional weights of atoms were rather philosophic than practical. They were concerned with the structure of individual atoms and so might be, and wisely were, set aside till the time, distant enough it would then have seemed, when these hypothetical entities could be dealt with experimentally.

The idea that atoms of the same element are all identical in weight could not be challenged by chemical methods, for the atoms are by definition chemically identical and numerical ratios were only to be obtained in such methods by the use of quantities of the element containing countless myriads of atoms. At the same time it is rather surprising, when we consider the complete absence of positive evidence in its support that no theoretical doubts were publicly expressed until late in the nineteenth century, first by Schutzenberger and then by Crookes, and that these doubts have been regarded, even up to the last few years, as speculative in the highest degree. In order to dismiss the idea that the atoms of such a familiar element as chlorine might not all be of the same weight, one had only to mention diffusion experiments and the constancy of chemical equivalents. It is only within the last few years that the lamentable weakness of such arguments has been exposed and it has been realized that the experimental separation of atoms differing from each other by as much as 10 per cent. in weight, is really an excessively difficult operation.

**3. Crookes' meta-elements.**—The chemist who above all others urged the possibility of the heterogeneity of atoms was the late Sir William Crookes, to whom we are indebted for so many remarkable scientific prophecies. His address to the Chemical Section of the British Association at Birmingham in 1886<sup>1</sup> is a most amazing effort of reason and imagination combined and should be read by all those interested in the history of scientific thought. In it he says: "I conceive, therefore, that when we say the atomic weight of, for instance, calcium is 40, we really express the fact that, while the majority of calcium atoms have an actual atomic weight of 40, there are not a few which are represented by 39 or 41, a less number by 38 or 42, and so on. We are here reminded of Newton's "old worn particles."

<sup>1</sup> Crookes, *Nature*, 34, 423, 1886.

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" Is it not possible, or even feasible, that these heavier and lighter atoms may have been in some cases subsequently sorted out by a process resembling chemical fractionation ? This sorting out may have taken place in part while atomic matter was condensing from the primal state of intense ignition, but also it may have been partly effected in geological ages by successive solutions and reprecipitations of the various earths.

" This may seem an audacious speculation, but I do not think it beyond the power of chemistry to test its feasibility."

Later<sup>1</sup> he developed this idea in connection with his pioneer work on the rare earths. By a laborious process of fractional precipitation he subdivided the earth yttria into a number of components which had different phosphorescent spectra but resembled each other very closely in their chemical properties. Pointing out that at that time yttrium was considered to be an element, he says : " Here, then, is a so-called element whose spectrum does not emanate equally from all its atoms ; but some atoms furnish some, other atoms others, of the lines and bands of the compound spectrum of the element. Hence the atoms of this element differ probably in weight, and certainly in the internal motions they undergo." He called such components " Meta-elements " and suggested that the idea might apply to the elements generally, for example, referring to the seven series of bands in the absorption spectrum of iodine, " some of these molecules may emit some of the series, others others, and in the jumble of all these molecules, to which is given the name 'iodine vapour,' the whole seven series are contributors."

In so far as they differed a little in atomic weight and a mixture of them constituted a chemical element, these hypothetical meta-elements may be said to have offered the first feasible explanation of the fractional atomic weights. But as more and more refined chemical methods were applied, the rare earths one after another yielded to analysis and the different spectra observed by Crookes were shown to be due to the fact that he was dealing with a mixture of real elements, each of which had a characteristic spectrum and a definite atomic weight. The theory of meta-elements was therefore abandoned and the problem of fractional atomic weight remained unsolved.

**4. The discovery of isotopes.**—As time went on the numbers representing the atomic weights grew more and more accurate and consistent. Significant figures one after another were added by one worker, confirmed by others, and finally approved by an International Committee. Small blame to the student therefore if, when studying

<sup>1</sup> Crookes, *Trans. Chem. Soc.*, 53, 487, 1888 ; 55, 257,

the imposing list of numbers called the International Atomic Weights, he fell into the very natural error of confusing "atomic weights" with "weights of atoms," and considered that these figures did actually represent the relative weights of the individual atoms themselves.

Why so many of the atomic weights should be very nearly integers when expressed on the scale  $O = 16$  was still a very difficult question to answer, for the probability against this being due to pure chance was enormous, but it was not until the discovery of radioactivity that the true reason for this curious jumble of whole numbers and fractions was suggested, and later confirmed generally by positive ray analysis. It is worth noting that the first experimental proof that the atoms of an element might be even approximately of the same weight was given by positive ray parabolas.<sup>1</sup>

The results given by the radioactive elements introduced a wealth of new and revolutionary ideas. One of these was that elements might exist which were chemically identical but yet differed in radioactive properties and even in atomic weight. By 1910 this idea had gained ground and was seriously put forward and discussed by Soddy. At about the same period the technique of positive ray analysis was rapidly being improved, and in 1912 the first results were obtained from neon which were later to support this new idea and carry it into the region of the non-radioactive elements. From this time onwards advances were made in the two fields side by side, and so it happened that at the meeting of the British Association in 1913<sup>2</sup> papers were read in different sections, one of the Radio-elements and the Periodic Law, the other on the Homogeneity of Neon, both of which tended to prove that substances could exist with identical, or practically identical, chemical and spectroscopic properties but different atomic weights.

The need for a specific name for such substances soon became imperative, and Soddy suggested the word Isotopes (*ἴσος*, equal, *τόπος*, place) because they occupied the same place in the periodic table of the elements.

**5.—Progress in the analysis of the non-radioactive elements.**—Immediately following the completion of the mass spectrograph definite proof of the existence of the isotopes of neon was published in November, 1919. A few weeks later the isotopic complexity of chlorine and mercury was demonstrated and the whole

<sup>1</sup> V. p. 26.

<sup>2</sup> Oddly enough, this was the first meeting of the Association at Birmingham since the one twenty-seven years before at which Crookes made his prophetic remarks about atomic weights already quoted.

## INTRODUCTION

number rule formulated, oxygen and carbon being taken as standard simple elements.

Progress in 1920 was rapid. In March the constitution of argon, helium, hydrogen, nitrogen and krypton was published together with a preliminary note on xenon. Boron, fluorine, silicon, bromine, sulphur, phosphorus and arsenic followed in July. Proof of the simple nature of iodine and confirmation of the five principal isotopes of xenon appeared in December, and in the same month Dempster announced his discovery of the isotopes of magnesium.

In February, 1921, the two isotopes of lithium were announced jointly by G. P. Thomson and the writer, and this result was confirmed by Dempster two months later. In the meanwhile the mass spectrograph had been successfully applied to the anode rays of sodium, potassium, rubidium and caesium, and these analyses were followed by that of nickel in June. In November, G. P. Thomson published results indicating that beryllium was a simple element, and a little later Dempster analysed calcium and zinc.

In June, 1922, largely owing to the valuable properties of schumannized plates, the complexity of tin was demonstrated, and the sixth and seventh isotopes of xenon were confirmed. Results for iron appeared in September and for selenium and aluminium in November. At the same time the probability of the existence of two additional rare isotopes of xenon was indicated. Antimony was analysed a few weeks later.

In 1923 the method of accelerated anode rays was worked out, and resulted in immediate success with many metallic elements. The first analysis of germanium was published in June, and that of copper in August. The analyses of ten more elements : scandium, titanium, vanadium, chromium, manganese, cobalt, gallium, strontium, yttrium and silver were announced at the British Association meeting in Liverpool in September.

In 1924 these results were extended to barium, lanthanum, praseodymium, neodymium, zirconium, cerium, cadmium, tellurium and bismuth. During the next four years attention was turned towards more accurate measurement of mass by means of the second mass spectrograph ; among the comparatively few new isotopes announced were those of mercury and ordinary lead. Additional isotopes of germanium and sulphur were found.

In 1929, owing to a new means of attack by analysis of the absorption spectra of the air, two rare isotopes of oxygen were announced by Giauque and Johnston. The first mass spectrum of uranium lead was also obtained. In 1930 chromium, molybdenum and tungsten were attacked successfully by means of their carbonyls and in

1931 osmium, ruthenium, rhenium, thallium and uranium were analysed.

In 1932 the simple constitution of niobium and tantalum was demonstrated and the hydrogen isotope of mass 2 was discovered by Urey. In 1933 improved anode ray technique applied to the second mass spectrograph enabled the rare earths to be tackled and neodymium samarium, europium, gadolinium and terbium were analysed. In 1934 all the other rare earths, dysprosium, holmium, erbium, thulium, ytterbium and lutecium followed. Results were obtained with hafnium and rhodium, and new isotopes of calcium and titanium discovered. A rare third isotope of argon was announced by de Gier and Zeeman.

In 1935 only four elements, platinum, palladium, gold and iridium remained, and all of these were analysed by Dempster, in that order, using his vacuum spark method. Since then a number of rarer isotopes have been found, and no doubt more will be, but so far as the identification of the main stable constituents of the elements are concerned, the work may be regarded as finished.

## CHAPTER II

### THE RADIOACTIVE ISOTOPES

**6. Chemical identities among the radioactive elements.**— Apart from the purely speculative considerations which have already been detailed, the theory of isotopes had its birth in the gigantic forward wave of human knowledge inaugurated by the discovery of radioactivity. It can admittedly be argued that, even if no radioactive elements existed, isotopes would inevitably have been discovered by the methods of mass ray analysis. But progress must then have been exceedingly slow, and the arrival at the real interpretation of the idea, depending as it does on Rutherford's theory of the "nucleus" atom, almost impossible.

In 1906 Boltwood at Yale discovered a new element in the radioactive group which he called Ionium,<sup>1</sup> and described as having chemical properties similar to those of thorium. So much was this the case that if, by accident, salts of these two elements were mixed, he found it impossible to separate them again by any of the chemical processes.

Boltwood, being occupied in the experimental proof that ionium was the parent substance of radium, did not pursue this line of investigation further at the time, but the work was later taken in hand by Marekwald and Keetman of Berlin.<sup>2</sup> Thanks to the rapid advance in radioactive methods there were now at command means of detecting change in concentration of a delicacy unheard of in the previous work on the rare earths, but yet, after years of patient and laborious work, not the slightest sign of separation of ionium and thorium could be observed. The chemical similarity between these two bodies was therefore of an order entirely different to that exhibited by the rare earth elements, and came as near absolute identity as the most critical mind could require.

This result was confirmed in the most rigorous manner by Auer v. Welsbach,<sup>3</sup> who was able to apply to the problem his valuable experience in work on the rare earths.

Furthermore, Mesothorium, discovered by Hahn in 1907, was

<sup>1</sup> Boltwood, *Amer. J. Sci.*, **22**, 537, 1906; **24**, 370, 1907.

<sup>2</sup> Keetman, *Jahr. Radioaktivitat*, **6**, 269, 1909.

<sup>3</sup> A. von Welsbach, *Wien. Ber.* **iia**, **119**, 1911, 1910.

shown to be chemically inseparable from radium by Marckwald<sup>1</sup> and Soddy<sup>2</sup> and similar chemical identities were shown to be exceedingly probable in many other cases of radioactive products. Certain regularities in the occurrence of these were pointed out by Hahn and Meitner.<sup>3</sup>

The situation was admirably summed up by Soddy in his report on radioactivity for the year 1910<sup>4</sup> in the following words:

"These regularities may prove to be the beginning of some embracing generalization, which will throw light, not only on radioactive processes, but on elements in general and the Periodic Law. Of course, the evidence of chemical identity is not of equal weight for all the preceding cases, but the complete identity of ionium, thorium and radiothorium, of radium and mesothorium I, of lead and radium D, may be considered thoroughly established. . . . The recognition that elements of different atomic weights may possess identical properties seems destined to have its most important application in the region of inactive elements, where the absence of a second radioactive nature makes it impossible for chemical identity to be individually detected. Chemical homogeneity is no longer a guarantee that any supposed element is not a mixture of several of different atomic weights, or that any atomic weight is not merely a mean number. The constancy of atomic weight, whatever the source of the material, is not a complete proof of homogeneity, for, as in the radio-elements, genetic relationships might have resulted in an initial constancy of proportion between the several individuals, which no subsequent natural or artificial chemical process would be able to disturb. If this is the case, the absence of simple numerical relationships between the atomic weights becomes a matter of course rather than one of surprise."

**7. Spectroscopic identity of isotopes.**—The next great advance was of an even more revolutionary character. This consisted in the demonstration that the chemically indistinguishable products of the transformation of the radioactive elements might also be spectroscopically identical. The idea that elements of different atomic weight might yet have the same spectrum appears to have been first entertained by A. S. Russell. With Rossi<sup>5</sup> he undertook the comparison between the spectrum of pure thorium and that of a mixture of thorium and ionium which radioactive evidence showed to contain a large percentage of the latter element. No new lines attributable to ionium

<sup>1</sup> Marckwald, *Ber. deutsch. Chem. Ges.*, **40**, 3420, 1910.

<sup>2</sup> Soddy, *Trans. Chem. Soc.*, **99**, 72, 1911.

<sup>3</sup> Hahn and Meitner, *Physikal. Zeitsch.*, **11**, 493, 1910.

<sup>4</sup> Soddy, *Ann Rep. Chem. Soc.*, **285**, 1910.

<sup>5</sup> Russell and Rossi, *Proc. Roy. Soc., A*, **77**, 478, 1912.

were observed ; in fact, the spectra obtained were absolutely indistinguishable.

After giving in full the radioactive evidence as to the probable percentage of ionium present, and showing that it was practically impossible for this to be too small for its spectrum to appear, the writers go on as follows :

" There are, however, two other possible ways of explaining our failure to obtain a distinct spectrum for ionium, besides the one discussed above. It is possible that :

- " (1) Ionium has no arc spectrum in the region investigated, or
- " (2) Ionium and thorium have identical spectra in the region investigated.

" The first possibility is highly improbable, for all solids of high atomic weights have arc spectra, and, further, all rare earths have highly complicated spectra.

" The second possibility, though somewhat speculative in nature, is suggested by some recent work on the chemical properties of the radio-elements. There is no evidence at present to disprove its truth. It is well known that there are no less than four sets of long lived radio-elements, the members of each of which are chemically non-separable. These elements do not all belong to the group of rare earths, many non-radioactive members of which are known to be chemically very similar. Mesothorium, for instance, which is chemically non-separable from radium, belongs to the alkaline earth group. Again, the two non-separable  $\alpha$ -ray products which are present in ordinary uranium, and which have been called by Geiger and Nuttall uranium I and uranium II belong to the chromium-molybdenum-tungsten group of elements. The explanation of these striking chemical similarities is very probably that the two very similar bodies are really different members of the same group of elements, the difference in their chemical properties being less pronounced than the difference between other members of the same group, owing to the small difference in their atomic weights. *But the possibility that they are identical in all physical and chemical properties, and differ only in atomic weight and in radioactive properties, should not be lost sight of. If this explanation should eventually prove justified, the spectrum of ionium would be identical with that of thorium."*

It is not surprising that the idea was put forward with some caution. Unlike that of chemical identity which had been led up to by a gradual series of steps, it was entirely new and contrary to all the preconceived ideas of the relations between the spectrum of an element and the masses of its atoms. The new departure was supported by Soddy<sup>1</sup>

<sup>1</sup> Soddy, *Chem. News*, Feb. 28, 1913.

but received some adverse criticism on the ground of insufficient evidence. The later work bearing on this point will be described in Chapters XIV and XV.

Already in 1911 the theory of the "Nucleus Atom"<sup>1</sup> had been formulated. This gave the first hint as to the physical meaning of chemical and spectroscopic identity, namely that the nuclei of atoms might vary in their mass but yet, at the same time, possess some property in common with each other, namely nuclear charge, upon which the chemistry and spectra depend.

In 1912 appeared the electrochemical work of Hevesy,<sup>2</sup> which led to the discovery of the remarkable field of research opened up by the use of radioactive bodies as indicators.<sup>3</sup> A little later Paneth and Hevesy were able to show the complete identity of the electro-chemical properties of Radium D and Lead.<sup>4</sup>

In 1914 Rutherford and Andrade<sup>5</sup> examined the self-excited X-ray spectrum of radium B. They used a crystal of rock salt for the analysis and got rid of the effect of the swift  $\beta$ -rays by putting the source in a strong magnetic field. The wave-length of the L radiation proved to be exactly that expected for lead from Moseley's experiment.<sup>6</sup> This was the first proof that isotopes had identical X-ray spectra. The actual values for ordinary lead were subsequently determined by Siegbahn and found to be in excellent agreement with Rutherford and Andrade's results.

**8. The Chemical Law of radioactive change.**—This law, put in the briefest form, asserts : A radioactive element when it loses an alpha particle goes back two places in the Periodic Table ; when it loses a beta particle it goes forward one place.

The law has been associated with the name of Soddy<sup>7</sup> who was the first to suggest, in the form of a valency property, that part of it relating to alpha rays.<sup>8</sup> But in its more complete enunciation, which took place early in 1913, at least four other investigators can claim a share.

Russell was the first to publish a law covering both kinds of rays,<sup>9</sup> but owing to the fact that he failed to realize that the sequence of

<sup>1</sup> V. p. 192.

<sup>2</sup> G. Hevesy, *Phil. Mag.*, **23**, 628, 1912 ; *Physikal. Zeitsch.*, **15**, 672, 715, 1912.

<sup>3</sup> V. p. 17.

<sup>4</sup> Paneth and Hevesy, *Sitzungber. K. Akad. Wiss. Wien, iiA*, **123**, 1037, 1913.

<sup>5</sup> Rutherford and Andrade, *Phil. Mag.*, **27**, 854, 1914.

<sup>6</sup> Moseley, *Phil. Mag.*, **26**, 1031, 1913.

<sup>7</sup> Stewart, *Recent Advances in Physical and Inorganic Chemistry*, Longmans, 1919.

<sup>8</sup> Soddy, *The Chemistry of the Radio Elements*, 29, First Edition, Longmans, 1911.

<sup>9</sup> Russell, *Chem. News*, Jan. 31, 1913.

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elements in the periodic table is a continuous expression, his statement was not so simple and definite as it might have been. Fajans,<sup>1</sup> using as foundation the electrochemical results of Hevesy,<sup>2</sup> and Soddy, working on the results of a very full chemical investigation carried out at his request by Fleck,<sup>3</sup> published the generalization in its full and complete form independently, and practically at the same time.

This law, which will be shown later to be a natural consequence of the much wider generalization of atomic number discovered by Moseley, has been of the greatest value in correlating the numerous products of radioactive change, and predicting with accuracy which of them will have identical properties. To the latter the name Isotopes was applied by Soddy in the following words: "The same algebraic sum of the positive and negative charges in the nucleus when the arithmetical sum is different gives what I call 'isotopes' or 'isotopic elements' because they occupy the same place in the periodic table. They are chemically identical, and save only as regards the relatively few physical properties which depend upon atomic mass directly, physically identical also." Any element which is the result of a series of changes involving the loss of twice as many beta particles as alpha particles must clearly be the isotope of the parent element, since it must inevitably, by the above law, reach the same place in the periodic table at the end of these operations.

**9. Isotopes and isobars.**—The meaning of the word isotope was originally quite clear and definite but, as is the case with so many new terms introduced into science, it has since been given a much wider and looser meaning than that intended by its originator. Instead of being restricted to the different atomic species comprising a single element it is now used to express any atomic species whatever.

Just as we can have elements of the same chemical properties but different atomic weights, so we can also have those of the same atomic weight but different chemical properties. These Stewart<sup>4</sup> called "Isobars." His original spelling in the paper cited was "isobares," to distinguish the term from that used in meteorology, but of late the final e has been dropped by common consent in current literature on the subject. Any product due to the loss of a beta ray (which has a negligible mass) must be an isobar of its parent substance, for, without change of mass, it has moved in the periodic table and so changed its chemical properties.

**10. The radioactive transformations.**—The radioactive ele-

<sup>1</sup> Fajans, *Physikal. Zeitsch.*, Feb. 15, 1913.

<sup>2</sup> Hevesy, *Physikal. Zeitsch.*, Jan. 15, 1913.

<sup>3</sup> Fleck, *Trans. Chem. Soc.*, 103, 381, 1052, 1913.

<sup>4</sup> Stewart, *Phil. Mag.*, 36, 326, 1918.

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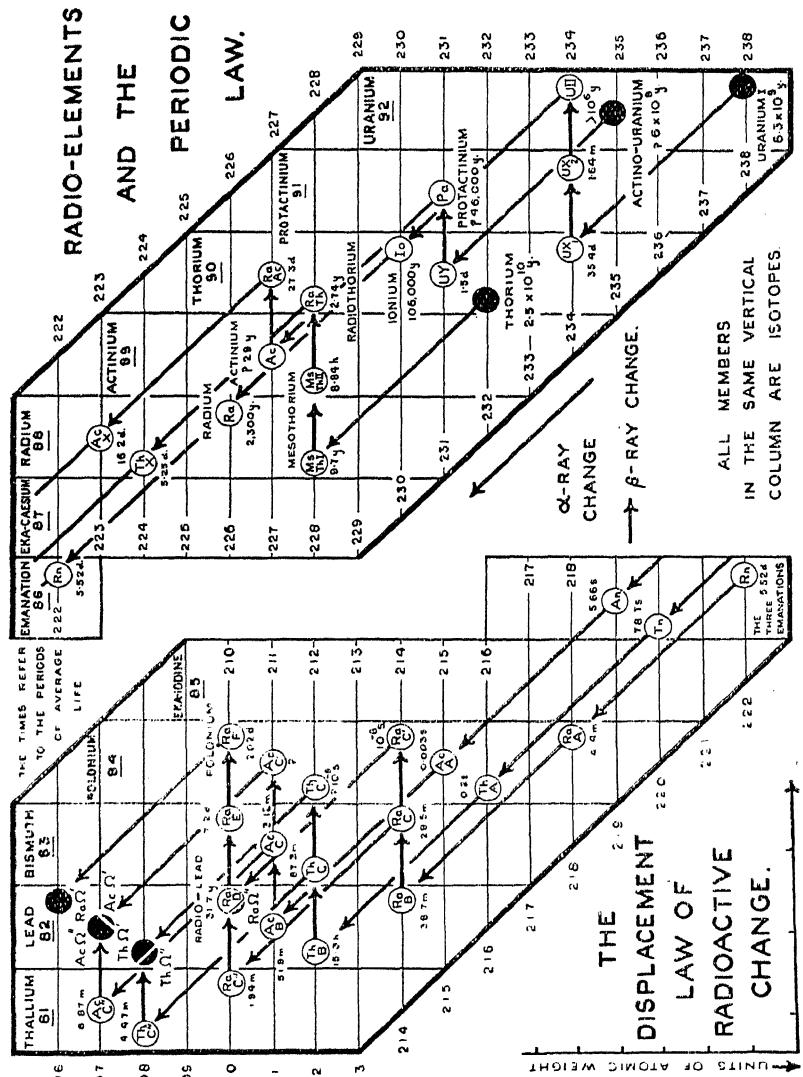


FIG. 1.

ments are all formed from the two parent elements uranium and thorium by a series of changes or transformations. These changes can be classified according to their nature into two types. In the first type of change called the  $\alpha$ -ray change the atom loses a particle of mass 4 carrying two positive charges ( $+ 2e$ ) which has been identified with the nucleus of the helium atom. In the second or  $\beta$ -ray change the particle shot off has a negligible mass and carries a single negative charge ( $- e$ ). Hence in an  $\alpha$ -ray change the element loses 4 units in atomic weight, while in a  $\beta$ -ray change its weight is unaltered.

The rate of decay of an element is measured by the "half value" period which may vary from  $10^{11}$  years to  $10^{-11}$  of a second, its connection with the velocity with which the rays are ejected together with the intricate researches by which the transformations have been explained belong to the subject of Radioactivity.<sup>1</sup> In connection with the discovery of isotopes it is enough to consider the results now accepted which are indicated in the two diagrams (Figs. 1 and 2).

In the first of these, which is due to Soddy,<sup>2</sup> the nuclear charge or Atomic number,<sup>3</sup> upon which all the chemical and spectroscopic properties of the elements depend, and which expresses its position in the periodic table, is indicated by a series of vertical columns edged with thick lines. The atomic weights are shown by fine horizontal lines. All elements lying in the same column will therefore be *isotopes* and all elements lying on the same line will be *isobars*. The  $\alpha$ - and  $\beta$ -ray changes are shown by arrows and the period of decay of the elements indicated by times expressed in suitable units.

The second diagram is arranged in a simple manner to show the general chains of transformation at a glance. In it the  $\alpha$ - and  $\beta$ -ray changes are plotted against atomic number and the other information omitted. On this diagram all elements lying on the same horizontal level will be isotopes. To take an example, uranium I which has an atomic number 92 and an atomic weight 238 loses one  $\alpha$ -particle and becomes uranium X<sub>1</sub>, atomic number 90, atomic weight 234. This then gives off two  $\beta$ -rays in succession, first becoming uranium X<sub>2</sub> and then uranium II. Uranium II has an atomic number 92 so that it is an isotope of uranium I. It has an atomic weight 234, so it is an isobar of uranium X<sub>1</sub> and uranium X<sub>2</sub>. Uranium II suffers an  $\alpha$ -ray change and is transformed into ionium, atomic weight 230, atomic number 90. Ionium loses an  $\alpha$ -particle and becomes radium, atomic weight 226. This by the same process changes to radium emanation, then to radium A, and then to radium B with atomic weight 214. We see that uranium II has lost 5  $\alpha$ -particles in succession, thereby coming

<sup>1</sup> Rutherford, Chadwick and Ellis, *Radiations from Radioactive Substances*.

<sup>2</sup> Soddy, *The Interpretation of the Atom*.

\* V. p. 194.

back 10 places, 92–82 in the periodic table, and its atomic weight has been reduced 20 units in the process. Radium B loses a  $\beta$ -particle, becoming radium C, which can disintegrate in two different ways. An extremely small proportion, 0·04 per cent., of its atoms undergo an  $\alpha$ -ray change to radium C<sub>2</sub> which then loses a  $\beta$ -particle and may become inactive lead of atomic weight 210. The vast majority of the atoms of radium C lose a  $\beta$ -particle and form radium C'. This next loses an  $\alpha$ -particle and becomes radium D, an active isotope of lead of atomic weight 210. Radium D now loses two  $\beta$ -particles in succession,

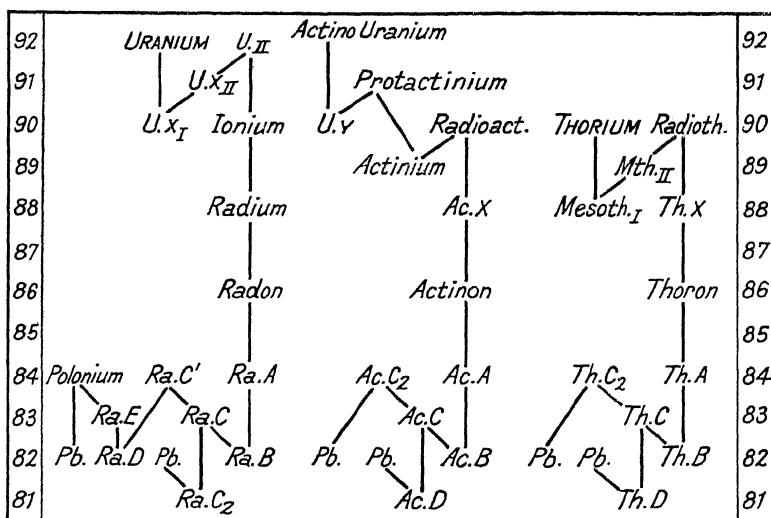


FIG. 2.—Diagram of the radioactive transformations in relation to atomic numbers. In every case a step two downwards is accompanied by the emission of an  $\alpha$ -particle and one upwards by a  $\beta$ -particle.

becoming radium E and then radium F, which is also called polonium. This finally undergoes its last  $\alpha$ -ray change and becomes inactive uranium lead of atomic weight 206.

The thorium and actinium chains can be followed on the diagrams in the same manner.

The final product of the actinium series is actinium lead of atomic weight 207.<sup>1</sup> Its origin is an isotope of uranium, actinouranium, of atomic weight 235.

**11. The atomic weight of lead.**—The theory of Isotopes, of which Professor Soddy had proved himself so prominent an advocate and defender, received its most triumphant vindication, as far as it concerned the products of radioactivity, at the hands of the very

<sup>1</sup> V. p. 186.

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chemists who had most reason to doubt its general application, the specialists in the determination of atomic weights.

The charts of radioactive disintegration show that the final product of every series is lead. If we take the main chain of the uranium-radium transformation this lead must have an atomic weight 206, for it has lost 5 alpha particles—each of weight 4—since it was radium, and the atomic weight of radium is 226. On the other hand, if we take the main thorium chain the lead end product must be 6 alpha particles lighter than thorium (232.15) and so should have an atomic weight about 208.

Now ordinary lead, from non-radioactive sources has an atomic weight 207.20, so Soddy<sup>1</sup> suggested in 1913 that the lead derived from minerals containing uranium but no thorium might have a smaller atomic weight than ordinary lead, and on the other hand the atomic weight of lead from minerals containing thorium but no uranium might be greater.

The first experiments were made by Soddy and Hyman<sup>2</sup> with a very small quantity of lead from Ceylon Thorite. This gave a perceptibly higher atomic weight than ordinary lead. Later a large quantity of the same mineral was available. The lead from this when carefully purified gave a density 0.26 per cent. higher than that of common lead. On the assumption that the atomic volumes of isotopes are equal this figure corresponds to an atomic weight of 207.74. A chemical atomic weight determination gave 207.694. A sample of the same lead was sent to Vienna where Professor Honigschmid, a well-known expert in such matters, obtained from it a value 207.77 as a mean of eight determinations. These figures not only showed that thorium lead had a higher atomic weight than ordinary lead but also that their atomic volumes were identical, as expected from theory.<sup>3</sup>

At the same time as this work was in progress, the leading American authority on atomic weights, T. W. Richards of Harvard, started a series of investigations on lead derived from various radioactive minerals.<sup>4</sup> The samples of lead from uranium minerals all gave results lower than ordinary lead, as was expected, and one particularly pure specimen of uranio-lead from Norwegian cleveite gave 206.08,<sup>5</sup> a very striking agreement with theory. Table I is taken from his Presidential address to the American Association at Baltimore, December, 1918.

<sup>1</sup> Soddy, *Ann. Rep. Chem. Soc.*, 269, 1913.

<sup>2</sup> Soddy and Hyman, *Trans. Chem. Soc.*, 105, 1402, 1914.

<sup>3</sup> Soddy, *Roy. Inst.*, May 18, 1917.

<sup>4</sup> Richards and Lembert, *J. Amer. Chem. Soc.*, 36, 1329, 1914.

<sup>5</sup> Richards and Wadsworth, *J. Amer. Chem. Soc.*, 38, 2613, 1916.

## USE OF RADIOACTIVE ISOTOPES AS INDICATORS 17

In further confirmation Maurice Curie in Paris<sup>1</sup> reported 206.36 for a lead from carnotite, and a still lower figure, 206.046, was obtained by Honigschmid in Vienna for a lead from the very pure crystallized pitchblende from Morogoro. The high value, 207.9, was also found by Honigschmid for lead from Norwegian thorite.<sup>2</sup>

TABLE I  
PROPERTIES OF DIFFERENT SAMPLES OF LEAD

	Common Lead.	Mixture Australian.	Uranio- Lead.	Percentage Difference.	
	A	B	C	A-B	A-C
Atomic weight . . . .	207.19	206.34	206.08	0.42	0.54
Density . . . .	11.337	11.280	11.273	0.42	0.56
Atomic volume . . . .	18.277	18.278	18.281	0.01	0.02
Melting point (absolute) .	600.53	600.59	—	0.01	—
Solubility (of nitrate) . .	37.281	37.130	—	0.41	—
Refractive Index (nitrate)	1.7815	1.7814	—	0.01	—
Thermoelectric effect . .	—	—	—	0.00	—
Spectrum wave-length . .	—	—	—	0.00	0.00

**12. Atomic weights of thorium and ionium.**—Although the above results obtained with lead are far the most conclusive and important it is not the only element which affords direct experimental evidence of the different atomic weights of isotopes. The atomic weight of ionium, calculated by adding the weight of one alpha particle to the atomic weight of its product, radium, is 230, whereas that of thorium, its isotope, is slightly above 232. Joachimsthal pitchblende contains hardly any thorium, so that an ionium-thorium preparation separated by Auer von Welsbach from 30 tons of this mineral might be regarded as containing a maximum concentration of ionium. On the other hand, the period of thorium is about  $10^5$  times longer than that of ionium so that it was doubtful if even in this preparation there would be enough ionium to show a difference in atomic weight. Honigschmid and Mlle Horovitz have made a special examination of this point, first redetermining as accurately as possible the atomic weight of thorium and then that of the thorium-ionium preparation from pitchblende. They found 232.12 for the atomic weight of thorium, and by the same careful method 231.51 for that of the thorium ionium.

**13. Use of radioactive isotopes as indicators.**—Consider an inactive element A which has a radioactive isotope B. If these are

<sup>1</sup> M. Curie, *Compt. Rend.*, **158**, 1676, 1914.

<sup>2</sup> Honigschmid, *Zeit. Elektrochem.*, **24**, 163, 1918; **25**, 91, 1919.

mixed together in any proportions no chemical or physical process known is capable of altering the ratio of the proportions of this mixture to any measurable extent. Now the radioactive methods of detecting and measuring B are many millions of millions of times more delicate than the chemical method of detecting and measuring A, so that by mixing with A a small quantity of B we can trace its presence far beyond the limits of chemical analysis. We have, as it were, marked the atoms of A with an indelible label so that the minutest trace of the element can be measured with ease and certainty.

By this powerful and novel device, which has been developed by G. Hevesy and F. Paneth<sup>1</sup> 10<sup>-9</sup> gr. of lead can be determined quantitatively and solution concentrations can be dealt with down to 10<sup>-11</sup> of normal. By adding radium D to the lead salt and estimating it electroscopically the solubility of lead sulphide and chromate, and the amount of lead chloride carried down in a silver chloride precipitate, may readily be determined.

Later, by the same principle, it was shown that a free exchange of the metallic atom among the competing acid radicles occurs for ionized, but not for non-ionized, compounds. The general method was to mix solutions of two different compounds of lead in equimolecular proportions, the one compound only being "activated" by presence of thorium B (which is isotopic with lead), and to determine the activity of the lead in the less soluble compound crystallizing out. When active lead nitrate and inactive lead chloride are dissolved in molecular proportion in boiling pyridine, the lead in the lead chloride crystallizing out is half as active as the lead in the original lead nitrate, but when such an active lead salt is so mixed with an organic compound of lead, such as lead tetraphenyl or diphenyl nitrate, in suitable solvents, no interchange of lead occurs, and the active lead salt retains its original activity. This constitutes something like a direct proof of the ionic dissociation theory and of the current views as to the difference between the nature of chemical union in electrolytes and non-electrolytes. When the acetates of quadrivalent activated lead and of bivalent inactive lead are mixed in glacial acetic acid, the activity of the first compound, after crystallizing out from the mixture, is reduced to one-half. This indicates, since the two lead ions differ only by two electrons, a free interchange of electrons between them and a dynamic equilibrium between ions and electrons and between free electrons and the electrodes in electrolysis.<sup>2</sup>

<sup>1</sup> Hevesy and Paneth, *Zeitsch. Anorg. Chem.*, 82, 323, 1913; Brit. Assoc. 1913; *Chem. News*, Oct. 13, 166, 1913.

<sup>2</sup> G. Hevesy and L. Zechmeister, *Ber.*, 53B, 410, 1920; *Zeitsch. Elektrochem.*, 26, 151, 1920.

Isotopes can also be used to determine the velocity of diffusion of molecules among themselves.<sup>1</sup> The rate of diffusion is dependent on the molecular diameter, and not on the mass, so that a radioactive element diffusing among the inactive molecules of its isotope affords a means of investigating this otherwise insoluble problem. The experiment has been tried with molten lead. At the bottom of a narrow vertical tube was placed a layer of lead rendered active by the presence of thorium B, and above it a layer three times the height of common lead. The whole was kept at 340° for several days. After cooling, the cylinder was cut into four equal lengths, each melted and hammered into foil, and the concentration of thorium B in each determined by alpha-ray measurements. Values for the diffusion coefficient between 1.77 and 2.54 per sq. cm. per day, with a mean of 2.22 in seventeen experiments, were obtained. On certain theories of physical chemistry this corresponds with a diameter of the lead molecule between 0.78 and  $1.16 \times 10^{-8}$  cm., according to the formulæ used to connect the two quantities. The value found by similar theories when reduced to a temperature of 18° and for a fluid of the viscosity of water, becomes 2.13. Since the diffusion coefficient of lead ions diffusing in aqueous solutions is 0.68, this indicates that the molecular diameter of metallic lead is only a third of that of the ion. The latter is probably hydrated.<sup>2</sup> In the same way the rate of diffusion of molecules among themselves has been measured in solid lead<sup>3</sup> and in lead chloride.<sup>4</sup> By the use of thorium B as an indicator the assimilation of lead from solutions by living plants has been investigated by Hevesy<sup>5</sup> with interesting results. The assimilated (radioactive) lead can be displaced by the introduction of the plant containing lead into another lead solution, whereby inactive lead atoms now take the place of the radioactive ones. From this it follows that the lead is not combined with carbon within the plant, but that it exists in the form of a dissociable salt which is soluble with difficulty.

With the help of radioactive indicators Paneth has been able to demonstrate the existence of metallic hydrides hitherto sought for without success. It has long been suspected that bismuth like its homologues, arsenic and antimony, should form a gaseous hydride, but the usual analytical tests were not sufficiently sensitive to prove this outright. The formation of this gas was demonstrated in the following way: A magnesium foil activated by thorium C, which is

<sup>1</sup> J. Groh and Hevesy, *Ann. Physik.*, IV, 63, 85, 1920.

<sup>2</sup> Soddy, *Chem. Soc. Ann. Rep.*, 227, 1920.

<sup>3</sup> Groh and Hevesy, *Ann. Physik.*, IV, 65, 216, 1921.

<sup>4</sup> Hevesy, *Zeitsch. Physik.*, 2, 148, 1920.

<sup>5</sup> Hevesy, *Biochem. J.*, 17, 439, 1923.

isotopic with bismuth, was dissolved in hydrochloric acid, and the hydrogen thus generated conducted into an emanation electrometer. The activity indicated by the electrometer proved that by this treatment several parts per thousand of the thorium C had been converted into a gaseous compound isotopic with bismuth hydride. In this way a practical knowledge of the best way of preparing the compound as well as an idea of its stability were obtained. With the help of this knowledge, the hydride was successfully made from ordinary bismuth in amounts sufficient to prove its existence by chemical methods. Lead hydride was discovered in a strictly analogous manner by first using a radioactive isotope, thorium B, to determine whether it existed and then verifying the result by using ordinary lead.<sup>1</sup>

A further application of radioactive indicators has been made to the problem of determining the magnitude of the adsorbing surface of powdered crystals.<sup>2</sup> For example, if powdered lead sulphate is shaken with a saturated solution of the same salt, the  $\text{PbSO}_4$  molecules on the surface of the powder are exchanged with those in the solution at a steady rate. If at the beginning of the experiment, thorium B (in the form of the sulphate) is added to the solution and kinetic equilibrium established, it is possible to determine the ratio between the  $\text{PbSO}_4$  molecules of the solution and those of the surface by measuring the decrease in the activity of the solution. Thus the number of molecules in the surface of the  $\text{PbSO}_4$  powder can be found. From this it can be calculated whether a known quantity of dyestuff adsorbed on this powder forms a layer one or more molecules thick. The investigations performed up to the present indicate that the layer of dyestuffs adsorbed on powdered crystals such as  $\text{PbSO}_4$ ,  $\text{PbCrO}_4$ , and  $\text{PbCl}_2$  is at the most only one molecule thick. This result is in good agreement with Langmuir's experiments on gaseous adsorption.

The discovery of transmutation has recently enabled the method to be extended to indicators made artificially, particularly radioactive phosphorus. This has opened up an entirely new means of attack on many biological problems. It is, however, beyond the scope of this book to do more than call attention to the brilliant series of researches in this field carried out by Hevesy and his school at Copenhagen.

<sup>1</sup> Paneth, *Zeitsch. Electrochem.*, **24**, 298, 1918; *Ber.*, **51**, 1704, 1918; *Zeitsch. f. Anorg. Chem.*, **35**, 549, 1922.

<sup>2</sup> Paneth, *Zeitsch. Electrochem.*, **28**, 113, 1922.

For further information the reader is referred to Paneth's book, *Radio-Elements as Indicators*, McGraw Hill, New York, 1928.

## CHAPTER III

### POSITIVE RAYS

**14. Nature of positive rays.**—Positive rays were discovered by Goldstein in 1886 in electrical discharge at low pressure. In some experiments with a perforated cathode he noticed streamers of light behind the perforations. This luminosity, he assumed, was due to rays of some sort which travelled in the opposite direction to the cathode rays and so passed through the apertures in the cathode; these he called “canalstrahlen.”<sup>1</sup> Subsequently Wien showed that they could be deflected by a magnetic field.<sup>2</sup> They have been very fully investigated in this country by Sir J. J. Thomson,<sup>3</sup> who called them Positive Rays on account of the fact that they normally carry a charge of positive electricity.

The conditions for the development of the rays are, briefly, ionization at low pressure in a strong electric field. Ionization, which may be due to collisions or radiation, means in its simplest case the detachment of one electron from a neutral atom. The two resulting fragments carry charges of electricity of equal quantity but of opposite sign. The negatively charged one is the electron, the atomic unit of negative electricity itself,<sup>4</sup> and is the same whatever the atom ionized. It is extremely light and therefore in the strong electric field rapidly attains a high velocity and becomes a cathode ray. The remaining fragment is clearly dependent on the nature of the atom ionized. It is immensely more massive than the electron, for the mass of the lightest atom, that of hydrogen, is about 1837 times that of the electron, and so will attain a much lower velocity under the action of the electric field. However, if the field is strong and the pressure so low that it does not collide with other atoms too frequently it will ultimately attain a high speed in a direction opposite to that of the detached electron, and become a “positive ray.” The simplest form of positive ray is therefore an atom of matter carrying

<sup>1</sup> Goldstein, *Berl. Ber.*, **39**, 691, 1886.

<sup>2</sup> Wien, *Verh. Phys. Gesell.*, **17**, 1898.

<sup>3</sup> J. J. Thomson, *Rays of Positive Electricity and their Application to Chemical Analyses*, Longmans, Green, 1913.

<sup>4</sup> R. A. Millikan, *The Electron*, University Chicago Press, 1918.

a positive charge and endowed, as a result of falling through a high potential, with sufficient energy to make its presence detectable.<sup>1</sup> Positive rays can be formed from molecules as well as atoms, so that it will at once be seen that any measurement of their mass will give us direct information as to the masses of atoms of elements and molecules of compounds, and that this information will refer to the atoms or molecules *individually*, not, as in chemistry, to the mean of an immense aggregate. It is on this account that the accurate analysis of positive rays is of such importance.

In order to investigate and analyse them it is necessary to obtain intense beams of the rays. This can be done in several ways. The one most generally available is by the use of the discharge in gases at low pressure.

**15. Mechanism of the electric discharge in gases at low pressure.**—It is a somewhat striking anomaly that while the working of the very recently invented "Coolidge" X-ray bulb can be simply described and explained, this is far from being the case with the much older ordinary "gas" tube. Notwithstanding the immense amount of research work done on the discharge at low pressures<sup>2</sup> many of its phenomena are not yet fully explained.

For the purposes of describing positive rays it is not necessary to consider the "striated discharge" or other phenomena connected with the anode end of the tube, but some ideas as to what is going on near the cathode will be a considerable help in our interpretation of the results of positive ray analysis and vice versa.

**16. The Crookes dark space.**—The comparatively dimly lit space in front of the cathode, terminating at the bright "negative glow" was first observed by Crookes. Its length is roughly inversely proportional to the pressure of the gas in the tube. Its boundary the edge of the negative glow is remarkably sharp in most gases, quite amazingly so in pure oxygen. If large plane cathodes are used so that the effect of the glass walls is minimized very accurate and consistent measurements can be obtained. Such measurements have been made under a great variety of conditions by the writer.<sup>3</sup> The

term "mass rays" has been suggested by Andrade (*The Structure of the Atom*, p. 83) to cover all swiftly moving particles of matter other than electrons. It therefore includes canalstrahlen, positive rays, anode rays, etc., each of which has a more limited scope.

<sup>2</sup> Compton and Langmuir, *Review of Modern Physics*, 2, 123, 1930; Sir J. J. Thomson and G. P. Thomson, *Conduction of Electricity through Gases*, 3rd ed., vol. 2.

<sup>3</sup> Aston, *Proc. Roy. Soc.*, A, 79, 80, 1907; Aston and Watson, *ibid.*, A, 86, 168, 1912; Aston, *ibid.*, A, 87, 428, 437, 1912.

distribution of electric force in the dark space has also been determined for large plane electrodes.<sup>1</sup>

In the theories on this subject many points are still obscure, but it seems fairly certain that ionization is going on at all points throughout the dark space, and that it reaches a very high intensity in the negative glow. This ionization is probably caused for the most part by electrons liberated from the surface of the cathode (Cathode Rays). These, when they reach a speed sufficient to ionize by collision, liberate more free electrons which, in their turn, become ionizing agents, so that the intensity of ionization from this cause will tend to increase as we move away from the cathode. The liberation of the original electrons from the surface of the cathode is generally regarded as due to the impact of positive ions (Positive Rays) generated in the negative glow and the dark space.

In addition to cathode ray ionization the positive rays travelling towards the cathode themselves are capable of ionizing the gas, and radiation may also play an important part in the same process. The surface of the cathode will therefore be under a continuous hail of positively charged particles. Their masses may be expected to vary from that of the lightest atom to that of the heaviest molecule capable of existence in the discharge tube, and their energies from an indefinitely small value to a maximum expressed by the product of the charge they carry  $\times$  the total potential applied to the electrodes. The latter is practically the same as the fall of potential across the dark space. If the cathode be pierced the rays pass through the aperture and form a stream heterogeneous both in mass and velocity which can be subjected to examination and analysis.

**17. Methods of detecting positive rays.**—The glow caused by the passage of the rays through rarefied gas led to their original discovery but is not made use of in accurate work. All the earlier investigations of the rays were made with screens of powdered willemite, which glows a faint green when struck by them, and as early as 1907 Sir J. J. Thomson made observations on hydrogen and helium rays by this means.<sup>2</sup> Dechend and Hammer<sup>3</sup> photographed the illuminated screen from the outside, but the real advance in technique was made in 1910 by recording the impact of the rays on a photographic sensitized surface introduced inside the evacuated apparatus. This device was first published by Koenigsberger and Kutschewski.<sup>4</sup>

<sup>1</sup> Aston, *ibid.*, A, 84, 526, 1911.

<sup>2</sup> J. J. Thomson, *Phil. Mag.*, 13, 561, 1907.

<sup>3</sup> Dechend and Hammer, *Proc. Heidelberg. Acad. Sci.*, 21, 12, 1910.

<sup>4</sup> Koenigsberger and Kutschewski, *Physikal. Zeitschrift*, 11, 666, 1910.

It was applied independently by Sir J. J. Thomson to his method of analysis with striking results.<sup>1</sup>

### 18. Sir J. J. Thomson's "parabola"<sup>2</sup> method of analysis.

—The method by which Sir J. J. Thomson made such a complete investigation into the properties of positive rays, and which still remains pre-eminent in respect to the variety of information it supplies, consists essentially in allowing the rays to pass through a very narrow tube and then analysing the fine beam so produced by electric and magnetic fields.

The construction of one of the types of apparatus used is indicated in Fig. 3. The discharge by which the rays are made takes place in a large flask A similar to an ordinary X-ray bulb of about  $1\frac{1}{2}$  litres capacity. The cathode B is placed in the neck of the bulb. Its

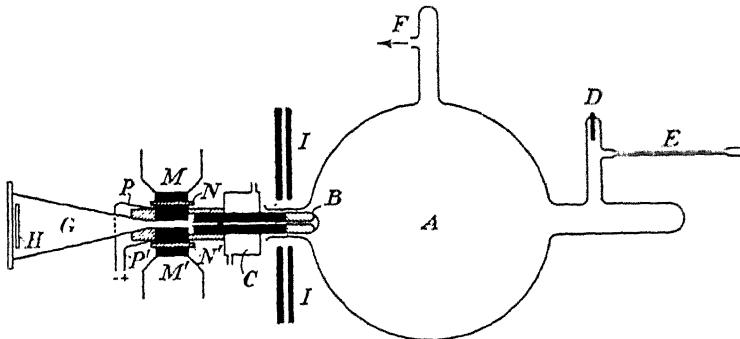


FIG. 3.—Positive Ray Apparatus.

face is made of aluminium, and so shaped that it presents to the bulb a hemispherical front provided in the centre with a funnel-shaped depression. This hole through which the rays pass is continued as an extremely fine-bore tube, usually of brass, about 7 cm. long, mounted in a thick iron tube forming the continuation of the cathode as indicated. The finer the bore of this tube the more accurate are

<sup>1</sup> J. J. Thomson, *Phil. Mag.*, **21**, 225, 1911.

<sup>2</sup> The possibilities of the parabola method have been thoroughly explored in recent years by Zeeman and his school in Holland. In 1934 they had their first spectacular success in the discovery of the rare isotope  $^{38}$  in argon, but since then their results, which are noted in Part III, have been less useful, and in several instances misleading. Their parabola photographs, obtained by the most skilful use of modern vacuum technique, are exceedingly beautiful and have an aesthetic, almost pyrotechnic, appeal to the imagination which is not possessed by the more prosaic lines of a mass spectrum; but unfortunately, owing to the inherent fault of inadequate resolving power, leading to deceptive photographic effects such as are discussed on p. 88, the parabola method is fundamentally unsuited to critical investigations of any but the lightest elements.

the results obtained, and tubes have been made with success as narrow as one-tenth of a millimetre, but as the intensity of the beam of rays falls off with the inverse fourth power of the diameter a practical limit is soon reached. The cathode is kept cool during the discharge by means of the water-jacket C.

The anode is an aluminium rod D, which is generally placed for convenience in a side tube. In order to ensure a supply of the gas under examination a steady stream is allowed to leak in through an exceedingly fine glass capillary tube E, and after circulating through the apparatus is pumped off at F by a Gaede rotating mercury pump. By varying the speed of the pump and the pressure in the gas-holder communicating with E, the pressure in the discharge tube may be varied at will and maintained at any desired value for considerable lengths of time. The pressure is usually adjusted so that the discharge potential is 30,000 to 50,000 volts. During the discharge all the conditions necessary for the production of positive rays are present in A. Under the influence of the enormous potentials they attain high speeds as they fly towards the cathode, and those falling axially pass right through the fine tube, emerging as a narrow beam.

This beam is subjected to analysis by causing it to pass between the pieces of soft iron P, P' which are placed between the poles M, M' of a powerful electromagnet. P and P' constitute the pole pieces of the magnet, but are electrically insulated from it by thin sheets of mica N, N', and so can be raised to any desired potential difference by means of the leads shown in the diagram. The rays then enter the highly exhausted "camera" G, and finally impinge upon the fluorescent screen or photographic plate H. In order that the stray magnetic field may not interfere with the main discharge in A, shields of soft iron, I, I' are interposed between the magnet and the bulb.

If there is no field between the plates, P, P' the beam of rays will strike the screen at a point in line with the fine tube called the undeflected spot. If an electric field of strength X is now applied between the plates a particle of mass  $m$ , charge  $e$ , moving with velocity  $v$ , will be deflected in the plane of the paper and will no longer strike the screen at the undeflected spot, but at a distance  $x$  from it. Simple dynamics show that if the angle of deflection is small  $x = k(Xe/mv^2)$ . In the same way, if the electric field is removed and a magnetic field of strength H applied between P and P' the particle will be deflected at right angles to the plane of the paper and strike the screen at a distance  $y$  from the undeflected spot where  $y = k'(He/mv)$ ,  $k$  and  $k'$  being constants depending solely on the dimensions and form of the apparatus used. If now, with the undeflected spot as origin, we take axes of co-ordinates OX, OY along

the lines of electric and magnetic deflection, when both fields are applied simultaneously the particle will strike the screen at the point  $(x, y)$  where  $y/x$  is a measure of its velocity and  $y^2/x$  is a measure of  $e/m$  its ratio of mass to charge.

Now  $e$  can only exist as the electronic charge  $4.80 \times 10^{-10}$  C.G.S. or a simple multiple of it. Thus if we have a beam of positive rays of constant mass, but moving with velocities varying over a considerable range,  $y^2/x$  will be constant and the locus of their impact with the screen will be a parabola  $pp'$  (Fig. 4). When other rays having a larger mass  $m'$  but the same charge are introduced into the beam, they will appear as another parabola  $qq'$  having a smaller magnetic displacement. If any straight line  $p, q, n$  be drawn parallel to the magnetic axis  $OY$  cutting the two parabolas and the electric axis  $OX$  in  $p, q, n$  it will be seen at once that  $m'/m = pn^2/qn^2$ . That is to say, the masses of two or more particles can be compared directly by merely measuring lengths the ratio of which is entirely independent of the form of the apparatus and the experimental conditions.

This is really the fundamental principle upon which the method is based. A photographic record is obtained on which we can identify at least one parabola as being associated with atoms or molecules of known mass; all the other parabolas

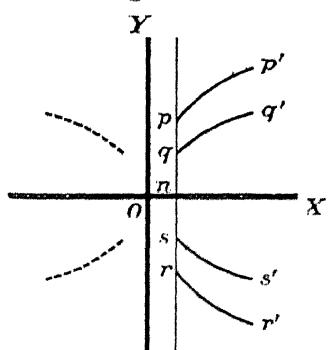


FIG. 4.—Positive Ray Parabolae.

can then be measured and compared with this one and their masses deduced. With electric and magnetic fields roughly known there is little difficulty in such an identification, and to make quite sure the absolute value of  $m/e$  for the hydrogen atom was determined and found to agree with the values obtained by other methods. In actual practice, since  $OX$  is an imaginary line and has no existence on the photograph, in order that the measurements may be made with greater convenience and accuracy the magnetic field is reversed during the second half of the exposure, when—in the case we are considering—two new parabolas will appear at  $rr'$ ,  $ss'$ , due to  $m$  and  $m'$  respectively; the masses can now be compared by the equation  $m'/m = pr^2/qs^2$ :  $p, q, r, s$  being any straight line cutting the curves approximately parallel to the magnetic axis. The measurement of these lengths is independent of zero determination, and if the curves are sharp can be carried out with considerable accuracy.

Some of the photographic results obtained by this method of analysis are shown in Plate I. The fact that the streaks are definite

sharp parabolas, and not mere blurs, was the first experimental proof that the atoms of the same element had very approximately the same mass.

It has been shown that the electrical displacement is in inverse proportion to the energy of the particle. Since this energy is simply dependent on and proportional to the electrical potential through which the charged particle fell before it reached the cathode and not upon its mass, the distribution of intensity along the parabolas will be somewhat similar. There will also be a definite maximum energy corresponding to the whole drop of potential across the discharge tube, with a corresponding minimum displacement on the plate; so that all normal parabolas will end fairly sharply at points  $p$ ,  $q$ , etc., equidistant from the magnetic axis OY. As the ionization is a maximum in the negative glow the parabolas are brightest at or near these points. The extension of the curves in the other direction, indicates the formation of ions at points in the discharge nearer the cathode which will so have fallen through a smaller potential.

**19. Secondary rays.**—As the pressure in the camera, though as low as possible, is never entirely negligible, the particles may make collisions, and so gain and lose electrons, while passing through the deflecting fields. This results in what Sir J. J. Thomson calls "secondary rays,"<sup>1</sup> which may be of a great many types. Some appear on the plate as general fog, others as straight beams seeming to radiate from the undeflected spot; these will easily be recognized on the photographs produced in Plate I. Secondary rays can produce parabolas which are very much like the genuine ones caused by particles which have retained their charge through both fields, and which may easily be mistaken for them unless special precautions are taken.

**20. Negatively charged rays.**—As there is intense ionization in the fine tube the charged particles may easily collide with and capture electrons in passing through it. A singly charged particle capturing a single electron will, of course, proceed as a neutral ray, and being unaffected by the fields will strike the screen at the central spot. If, however, it makes a second collision and capture it will become a negatively charged ray. Rays of this kind will suffer deflection in both fields in the opposite direction to the normal ones, and will therefore give rise to parabolas of a similar nature but situated in the opposite quadrants, as indicated by the dotted lines in the figure. Such negative parabolas are always less intense than the corresponding normal ones, and are usually associated with the atoms of electronegative elements such as carbon, oxygen, chlorine, etc.

The negative parabolas of H, C and O can be seen in the photographs. Plate I (1) and (2).

<sup>1</sup> J. J. Thomson, *Rays of Positive Electricity*, p. 32.

**21. Rays with multiple charges.**—If during ionization more than one electron is split off, the resulting positive ray will have a double or multiple charge. Taking the case of a doubly charged particle it may give rise to two distinct effects. In the first place, if it retains its double charge while passing through the analysing fields its behaviour will be quite indistinguishable from that of a normal ray of half its mass. Thus the effective mass of the doubly charged oxygen atom, written<sup>1</sup>  $O^{++}$ , will be 8. Parabolas due to  $C^{++}$  and  $O^{++}$  can be seen in Plate I (2). In the second place, the particle may retain its double charge through the whole potential fall of the discharge but capture an electron in the fine tube. It will then constitute a ray of normal ratio of mass to charge but with double the normal energy, so that the normal end of the parabolas will be extended towards the axis OY to a point half-way between that axis and the line  $pq$ . Such extensions will be seen on the bright parabolas due to carbon and oxygen in the photographs reproduced in Plate I.

Most elements are capable of losing two electrons, some, such as krypton, three or more, while mercury can lose no less than eight at a time. The results of the multiple charge on atoms of mercury is beautifully illustrated in Plate I (3). The parabola  $\alpha$  corresponding to normal single charge will be seen extended almost to the origin itself, while above a series of parabolas of diminishing intensity  $\beta$ ,  $\gamma$ , etc., indicate the atoms which have retained two, three or more charges.

**22. Dempster's method of positive ray analysis.**—It is clear from the considerations on page 26 that if the positive particles all fell through the same potential and so possessed the same energy, a magnetic field alone would suffice to perform their analysis with regard to mass. A method of analysis based on this idea was devised by Dempster at the Ryerson Physical Laboratory, Chicago.<sup>2</sup>

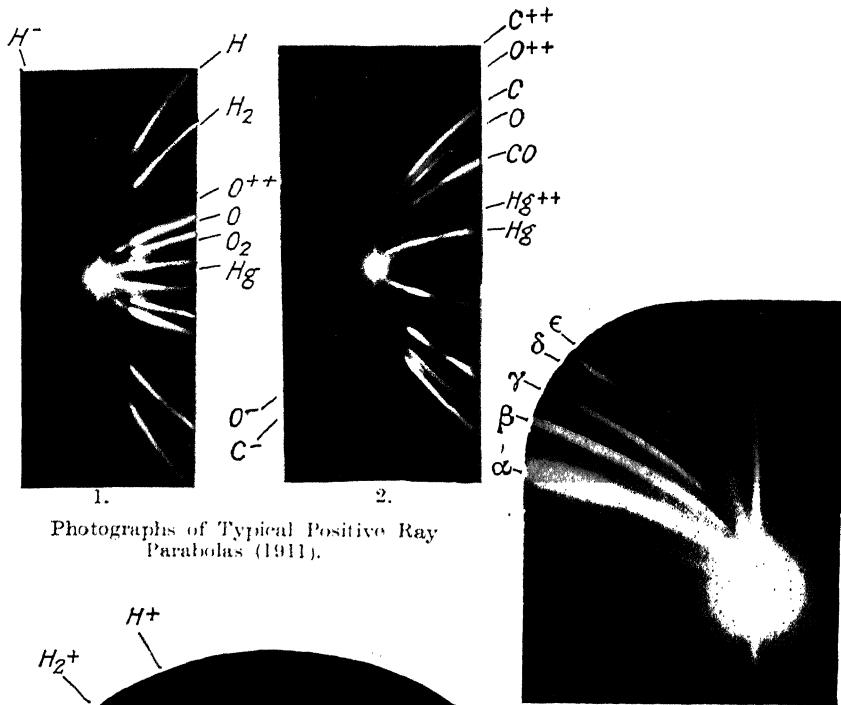
The method is essentially identical with that used by Classen in his determination of  $e/m$  for electrons.<sup>3</sup> The charged particles from some source fall through a definite potential difference. A narrow bundle is separated out by a slit and is bent into a semicircle by a strong magnetic field; the rays then pass through a second slit and fall on a plate connected to an electrometer. The potential difference  $P$ , magnetic field  $H$ , and radius of curvature  $r$  determine the ratio of the charge to the mass of the particle by the formula  $\frac{e}{m} = \frac{2P}{H^2r^2}$ .

The apparatus consisted of a glass tube G, Fig. 5, where the positive particles fell through a definite potential difference, and the

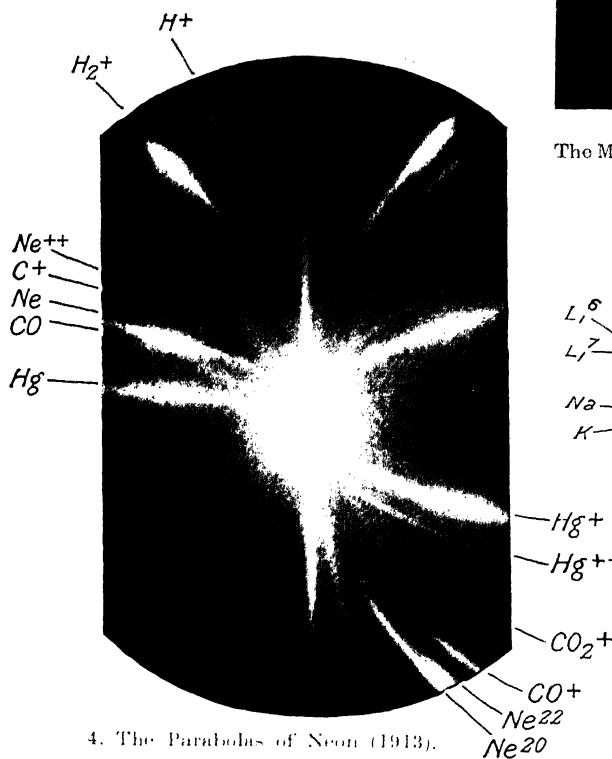
<sup>1</sup> In the normal singly-charged ray the plus sign is omitted for convenience.

<sup>2</sup> Dempster, *Phys. Rev.*, **11**, 316, 1918.

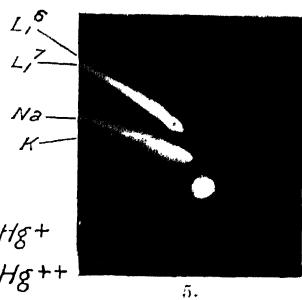
<sup>3</sup> Classen, *Jahrb. Hamburg Wiss. Anst.*, Beiheft, 1907.



Photographs of Typical Positive Ray  
Parabolae (1911).



4. The Parabolae of Neon (1913).



5. The Parabolae of  
Lithium (1921).



analysing chamber A, in which a strong magnetic field was produced between two semicircular iron plates 2·8 cm. thick and 13 cm. in diameter. The iron plates were soldered into half of a heavy brass tube B, so as to leave a passage or slot 4 mm. wide between the plates. A brass plate C closed this slot except for three openings into which short brass tubes were soldered. The glass tube G fitted into the first opening and a tube for exhausting into the second. The electrometer connection passed to a receiving plate through an ebonite plug E which formed a ground conical joint with the third brass tube. The two openings for the rays had adjustable slits  $S_1$ ,  $S_2$ , and a screen D was introduced into the analysing chamber to prevent reflected rays getting into the second slit. The whole was placed between the poles of a powerful electromagnet.

The accelerating potential P was applied by means of a large battery and was from 500 to 1750 volts or thereabouts. The experimental procedure consisted in maintaining a constant magnetic field and plotting the ionic current, measured by the electrometer, against the potential. The peaks on the curve corresponded to definite values of  $m/e$ , measured by the potential, and their heights to the relative quantities of the particles present in the beam.

The method is limited in its application by the fact that the ions must be generated with a velocity negligible compared with that produced by the accelerating potential. The first results were obtained from ions produced by heating salts on platinum strips, or by bombarding them with electrons. It was shown that the ions given off from heated aluminium phosphate consisted for the most part of sodium and potassium atoms, and that these had masses 23 and 39 respectively. The resolution possible with the first apparatus was claimed to be about 1 in 100. Dempster's successful application of this method to the analysis of complex elements will be described in a later chapter.<sup>1</sup>

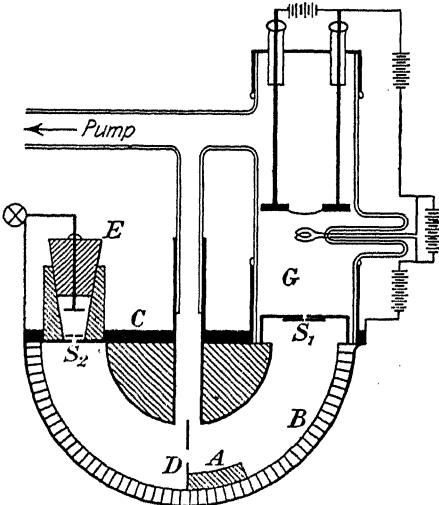


FIG. 5.—Dempster's Apparatus (1918).

<sup>1</sup> V. p. 70.

## CHAPTER IV

### NEON

**23. Positive ray analysis of neon.**—It is a curious and interesting point that while the first suggestion of the possibility of the occurrence of isotopes was obtained from the rarest of all substances in the earth's surface—the radioactive elements and their products—so the first result indicating the possibility of isotopes among the stable elements was yielded by neon, a gas of which, in a purified state, there was probably less than one gramme in existence.

Neon is one of the inactive constituents of the atmosphere, in which it occurs to the extent of 0·00123 per cent. by volume. It was first isolated by Ramsay and Travers in 1898, and was accepted as an elementary monatomic element of the helium group. Its density was measured with extreme care by Watson<sup>1</sup> and found to correspond with an atomic weight 20·200 ( $O = 16$ ), so that it is the lightest element whose atomic weight differs from a whole number in an unmistakable manner.

In the summer of 1912 there had been constructed in the Cavendish Laboratory a Positive Ray apparatus which was a considerable improvement on those made previously.<sup>2</sup> The parabolas corresponding to masses differing by 10 per cent. could be clearly resolved and distinguished by its means. Many gases were submitted to analysis; but no results were obtained which could not be accounted for until in November of that year a sample of the lighter constituents of air was introduced. In describing the results obtained one cannot do better than quote Sir J. J. Thomson's own words from his address to the Royal Institution on Friday, January 17, 1913.

"I now turn to the photograph of the lighter constituents; here we find the lines of helium, of neon (very strong), of argon, and in addition there is a line corresponding to an atomic weight 22, which cannot be identified with the line due to any known gas. I thought at first that this line, since its atomic weight is one-half that of  $CO_2$ , must be due to a carbonic acid molecule with a double charge of electricity, and on some of the plates a faint line at 44 could be detected.

<sup>1</sup> Watson, *Trans. Chem. Soc.*, **1**, 810, 1910.

<sup>2</sup> J. J. Thomson, *Rays of Positive Electricity*, p. 20.

On passing the gas slowly through tubes immersed in liquid air the line at 44 completely disappeared, while the brightness of the one at 22 was not affected.

"The origin of this line presents many points of interest; there are no known gaseous compounds of any of the recognized elements which have this molecular weight. Again, if we accept Mendeléeff's Periodic Law, there is no room for a new element with this atomic weight. The fact that this line is bright in the sample when the neon line is extraordinarily bright, and invisible in the other when the neon is comparatively feeble, suggests that it may possibly be a compound of neon and hydrogen,  $\text{NeH}_2$ , though no direct evidence of the combination of these inert gases has hitherto been found. I have two photographs of the discharge through helium in which there is a strong line, 6, which could be explained by the compound  $\text{HeH}_2$ , but, as I have never again been able to get these lines, I do not wish to lay much stress on this point. There is, however, the possibility that we may be interpreting Mendeléeff's law too rigidly, and that in the neighbourhood of the atomic weight of neon there may be a group of two or more elements with similar properties, just as in another part of the table we have the group iron, nickel, and cobalt. From the relative intensities of the 22 line and the neon line we may conclude that the quantity of the gas giving the 22 line is only a small fraction of the quantity of neon."

Other samples of gas containing neon all gave similar results. By good fortune some of the purest neon in existence was also available; this had been employed by the writer and Watson in some investigations on the Crookes Dark Space<sup>1</sup> and was actually a part of that by which the atomic weight had been determined. This sample also yielded the two separate parabolas with the same relative intensity as the others. One of the photographs taken with neon is reproduced in Plate I (4).

The last result proved that the most careful purification had not appreciably altered the intensity ratio between the lines and might at first sight appear a strong argument for the  $\text{NeH}_2$  explanation, but further study of the parabolas only added more weight to the chemical objections against the existence of such a compound. The only other alternative was a novel and revolutionary one, namely that neon could exist in two forms and that the relation between these was precisely that which had been described by Soddy a short time before as existing between the chemically inseparable radio-elements.

These considerations led the author to undertake a searching in-

<sup>1</sup> Aston and Watson, *Proc. Roy. Soc., A*, **86**, 1912.

vestigation on the constitution of the gas by two distinct lines of attack, first attempts at separation, secondly examination by positive rays.<sup>1</sup>

**24. Apparatus for the determination of density.**—As neon is chemically inactive the most satisfactory proof of a partial separation of its constituents is a change in density. It was therefore necessary to devise some means of determining density accurately, quickly and with the minimum quantity of gas. All these desiderata were obtained by the construction of a simple quartz micro-balance shown in Fig. 6.<sup>2</sup>

The principle upon which this works is that if a sealed vacuous quartz bulb is equilibrated against a solid piece of quartz on a balance the system can only be exactly balanced, at any predetermined position, when it is immersed in a fluid of an absolutely definite density; if the density is too high the bulb will be buoyed up, if too low it will

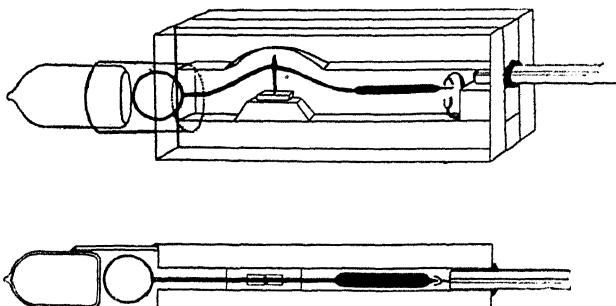


FIG. 6.—Micro-balance.

sink. We can therefore compare the densities of a known and an unknown gas by introducing them successively into the balance case and determining the pressures at which the system is exactly balanced.

The moving part of the balance is made entirely of fused quartz (shown black). It turns upon a single knife-edge cut on a piece of quartz rod about 0.5 mm. thick. To this rod, a few millimetres above the knife-edge, are fused two others about the same thickness forming the arms of the beam. To the end of one arm is fused a sealed vacuous quartz bulb holding about 0.3 c.c. and to the other a counterpoise made of a piece of rod about 2 mm. thick. The beam is supported by its knife-edge on a horizontal quartz plate and housed in a thick glass vacuum-tight case fitting as closely as possible so that its volume is a minimum. The case is connected through the capillary tube shown to a gas pipette and a pump for the introduction and removal

<sup>1</sup> The neon necessary for this research was given by M. Georges Claude of Paris.

<sup>2</sup> Aston, *Proc. Roy. Soc., A*, 89, 440, 1914.

of gas and also to a simple form of mercury manometer. The beam was adjusted during its construction so that it balanced in air at about 85 mm. pressure. In the process of adjustment the end of the counterpoise was drawn out into a fine tail ending in a small knob ; this was used as the pointer of the beam. The sensitivity of the balance is about  $10^{-6}$  mgrm., which enables the manometer to be set to one-twentieth of a millimetre with ease.

**25. Method of using the density balance.**—About the right volume of gas, generally known from previous experience, is admitted to the balance case and the mercury level in the manometer slowly raised (increasing the pressure in the balance case) until the bulb rises and the knob at the extremity of the counterpoise appears on the field of a fixed reading microscope. The pressure is then carefully adjusted until the knob reaches some definite arbitrary zero point and shows no tendency to move. The pressure is then read off. The gas is now pumped off and the same operation repeated with a gas of known density such as pure oxygen. The ratio of the densities is clearly the inverse of the pressures read, and as the latter are low the molecular weight is given direct without any corrections being required.

Difficulties connected with temperature, so serious in density determinations on the usual scale, are eliminated for so minute is the quantity of gas (about 0.0005 grm.) used that when this is compressed inside the massive walls of the balance case thermal equilibrium is almost instantaneous. The whole operation of determining the density of a gas to 0.1 per cent. can be completed in ten minutes. Only about half a cubic centimetre of the gas is required for the operation.

**26. Experiments on separation by distillation.**—The first attempt at separation was made by continual fractionation over charcoal cooled in liquid air. The apparatus used is illustrated in the accompanying figure ; the method of working was as follows :

The gas was admitted in *a*, one of the small charcoal bulbs, *a*, *b*, *c*, *d*, all cooled in liquid air. After a reasonable time had elapsed the first fraction was pumped off by lowering mercury in gas-holder A and opening the connecting stopcock between it and *a*. After another interval the stopcock was turned, the mercury raised in A and the gas forced into bulb *b*. The mercury was next lowered in both A and B, the former receiving the second fraction from *a* while the latter withdrew the first fraction of the gas now in *b*. The fundamental assumption on which this arrangement was made was that at this stage, if the vapour-pressures of the gases are nearly the same, the gas in A would have the same composition as that left in *b*, and that they therefore might be mixed. This was done by raising the mercury, which not only drove the gas from A into *b* but also the

lightest fraction from B into *c*, where it again fractionated, each process driving the lower boiling gas forward and keeping the higher back.

The apparatus may contain any number of units, the whole system being made cyclical and continuous by joining the charcoal bulb at one end with the gas-holder at the other. Four such units were actually employed, and after four operations the liquid air was removed from *a* and the residue it contained was pumped off completely with an Antropoff pump as the first contribution to the heaviest fraction; in the same way that in D was also pumped off as that of the lightest. The bulb *a* was then immersed again in liquid air and the process continued.

After about two-thirds of the gas had been collected in this way as light and heavy fractions, that remaining was all pumped out as

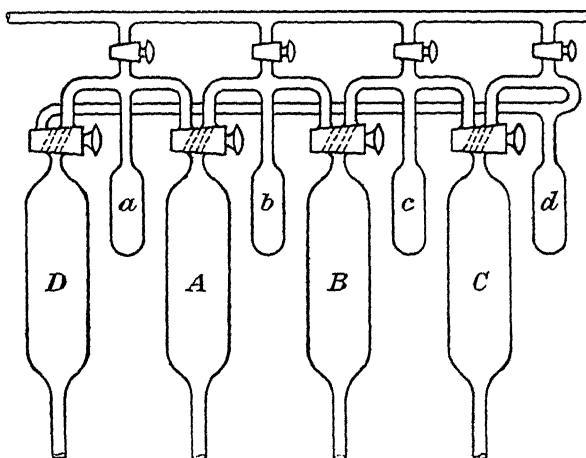


FIG. 7.—Fractionation Apparatus.

the middle fraction. The process was next repeated with the light and heavy fractions in turn, the intermediate ones being combined by a definite rule.

By this arrangement, which does many operations at once, the small quantity of helium contained in the original gas was removed in a remarkably short time, after which the neon was subjected to continual fractionation for three weeks. The gas had now been through about 3000 fractionations and was divided into seven main fractions; the densities of these were determined in order by the quartz micro-balance starting with the lightest, the figures for the pressures giving the same zero as oxygen at 76.35 were as follows:

(1)	(2)	(3)	(4)	(5)	(6)	(7)
121.05	120.95	121.05	120.90	121.00	121.05	121.05

The mean of these, 121.00, gives a molecular weight of 20.19, which is identical within experimental error with the accepted one of 20.200 determined by Watson. It was evident that no appreciable separation had been achieved.

A positive ray photograph was taken of the two extreme fractions and this showed no appreciable change in the relative intensity of the two parabolas. It was, however, a very good one for the purpose of measurement and a careful comparison of their displacements with those of the known lines due to CO and CO<sub>2</sub> showed, with a probability almost amounting to certainty, that the atomic weight of the lighter was not as great as 20.20.

Encouraged by this evidence it was decided to make a further attempt at separation by the method of fractional diffusion.

**27. Experiments on separation by diffusion.**—The first apparatus used was much the same as that described by Ramsay and Collie in their work on the diffusion of argon and helium.<sup>1</sup> The diffusion was carried out at a low pressure and the plug was made of two short lengths of clay pipe in series.

The method of fractionation was that described by Travers.<sup>2</sup> About 100 c.c. of neon was divided first into seven and later into eight fractions. The complete series of fractionations was repeated fifteen times, after which the two extreme fractions were roughly purified over charcoal and their densities measured. These indicated a difference of about a half per cent., a very hopeful result—moreover the lighter fraction showed no appreciable quantity of helium even when analysed by the method of positive rays which is much more delicate than the spectroscope for this purpose.

The extremely laborious process was again taken in hand and the fractionation repeated another twenty-one times, at the end of which the whole of the lightest fraction was lost by a most unfortunate accident. This was the more serious as the two extreme fractions had been systematically enlarged with a view to fractionating each separately.

Despite this set-back the fractionation of the heaviest 20 c.c. was proceeded with. This was divided into five fractions and fractionated ten times. The next lightest fraction to the one lost was taken, divided into five parts and fractionated twelve times. These very tedious operations were now brought to a close and the two extreme fractions of 2 to 3 c.c. each were purified over charcoal with the greatest possible care.

The final densities which further purification failed to alter were

<sup>1</sup> Ramsay and Collie, *Proc. Roy. Soc., A*, **60**, 206, 1896.

<sup>2</sup> Travers, *A Study of Gases*, p. 289.

20.15 and 20.28 (Oxygen = 32). This change in density is small but it is much too marked to be ascribed to contamination or to experimental error. Looked at in the light of modern knowledge there can be no reasonable doubt that partial separation had been actually achieved. The extent of the separation is about that to be expected from the theoretical considerations of separation by diffusion given on page 245. A spectroscopic examination of these two fractions showed no appreciable difference between them.

These results were announced at the meeting of the British Association at Birmingham in 1913 and at the same time the evidence afforded by the positive ray photographs discussed. This is available from three distinct considerations : the character of the lines, their position and their intensity. A careful examination of the plates showed, when proper allowance had been made for difference of intensity, that the two parabolas had characteristics identical with one another. Both were prolonged towards the vertical axis showing that the particles causing them were equally capable of carrying more than one charge.<sup>1</sup> Now up to that time no cases of multiple charges had been found to occur on molecules, but only on atoms. One was therefore led to infer that both lines were due to elements.

Measurements of the position of the parabolas relative to those of CO and other known bodies in the discharge tube gave consistent results, indicating that the lighter of the two corresponded with an atomic weight less than 20.2, but the accuracy was not sufficient to make this certain. The relative intensity of the parabolas was estimated by three independent observers as about 10 to 1. Its apparent invariability was valuable corroborative evidence against the possibility of the 22 line being due to the presence of other gases in the discharge tube.

**28. Second attempt at separation by diffusion.**—In order to carry out further diffusion experiments an elaborate automatic diffusion apparatus was devised so as to avoid the excessive labour of working by hand. This worked on the see-saw principle and dealt with 300 c.c. of neon at a time. It was started in 1914, but as it had little success in its object there is no need to describe it in detail. It will be enough to say that although it performed the mechanical operations of diffusion many thousands of times in a satisfactory manner the separation achieved was exceedingly poor—actually only about half that attained previously. This disappointing result was undoubtedly due to the mistake made in designing it to carry out the diffusion at atmospheric pressure, for under these conditions the “mixing” is very bad.<sup>2</sup>

When the work was interrupted by the War it could be said that

<sup>1</sup> V. p. 28.

<sup>2</sup> V. p. 244.

although the presence of two isotopes in neon was indicated by several lines of reasoning, none of these could be said to carry absolute conviction.

**29. The analysis of neon by the mass spectrograph.**—By the time the work was resumed the existence of isotopes among the products of radioactivity had been put beyond all reasonable doubt by the work on the atomic weight of lead<sup>1</sup> and was accepted generally. This fact automatically increased both the value of the evidence of the complex nature of neon and the urgency of its definite confirmation. It was realized that separation could only be very partial at the best and that the most satisfactory proof would be afforded by measurements of atomic weight by the method of positive rays. These would have to be so accurate as to prove beyond dispute that the accepted atomic weight lay between the real atomic weights of the constituents, but corresponded with neither of them.

No apparatus then in existence appeared to be adequate to carry this out. Sir J. J. Thomson had already announced at a Royal Institution lecture in 1918<sup>2</sup> that he had examined chlorine by the parabola method and had come to the conclusion that this element was "normal," that is that it gave a single parabola at the position corresponding to its chemical atomic weight. This erroneous conclusion, naturally not stressed during his lifetime, is interesting historically and because it does something to explain his critical attitude when he subsequently opened the discussion on isotopes at the Royal Society.<sup>3</sup>

Well aware of the weak points of the parabola method, and greatly assisted by experience gained in working with it from 1910 to 1913, the writer was able to work out a new and more powerful method of analysis which will be described in the next chapter, and apparatus to apply this was constructed in the Cavendish Laboratory on his return there in 1919. This proved amply accurate enough for the purpose, and the results obtained with neon<sup>4</sup> showed beyond doubt that this element was a mixture of two constituents which corresponded in every particular with Soddy's isotopes and had whole number atomic weights 20 and 22.

<sup>1</sup> V. p. 16.

<sup>2</sup> *Engineering*, Mar. 29, 345, 1918.

<sup>3</sup> *Proc. Roy. Soc., A*, 99, 87, 1921.

<sup>4</sup> Aston, *Phil. Mag.*, 39, 449, 1920.

## CHAPTER V

### THE FIRST MASS SPECTROGRAPH<sup>1</sup>

**30. Limitations of the parabola method.**—The parabola method of analysis of positive rays described in Chapter III, though almost ideal for a general survey of masses and velocities, has objections as a method of precision; many rays are lost by collision in the narrow canal-ray tube, the mean pressure in which must be at least half that in the discharge bulb; very fine tubes silt up by disintegration under bombardment; the total energy available for photography falls off as the fourth power of the diameter of the canal-ray tube.

The first two objections can be overcome, as will be described below, by replacing the brass or copper tube by fine apertures made in aluminium, a metal which appears to suffer little disintegration, and by exhausting the space between these apertures to the highest degree by means of a subsidiary charcoal tube or pump. The falling off in intensity of the parabolas as one attempts to make them finer is a very serious difficulty, as the accuracy and resolving power depend on the ratio of the thickness to the total magnetic deflexion; and if we increase the latter the electric deflexion must be increased to correspond and the parabolas are drawn out, resulting again in loss of intensity.

Also, the nature of the patch thrown on the plate by the use of a long circular tube will clearly be the same as that caused by the light from an evenly illuminated disc passing through a circular aperture of the same diameter, that is to say it will have a penumbra. Similarly the parabolic streak produced by an infinite series of such patches will not be particularly suitable for accurate measurements as it has no definite edges.

<sup>1</sup> Like the word "isotope" noted on p. 12 the word "mass spectrograph" has lost the original restrictions intended by the writer when he introduced it in 1920, and is now loosely applied to any method of positive ray analysis, even, by a quite unnecessary anachronism, to the parabola method. It is best restricted to those forms of apparatus capable of producing a focused mass spectrum of lines on a photographic plate. An apparatus in which the focused beam of rays is brought up to a fixed slit, and there detected and measured electrically is best termed a "mass spectrometer." The first of these was devised by Dempster as shown in Fig. 5, though the term was not introduced till much later (*V. p. 97*).

**31. Methods of increasing the intensity of the spot.**—The concentration of the stream of positive rays down the axis of the discharge bulb is very marked, but there is good evidence for assuming that the intense part of the stream occupies a considerable solid angle. This suggests the possibility of an increase of intensity by means of a device which should select the rays aimed at a particular spot on the plate, whatever direction they come from. For example, a thin gap between two coaxial equiangular cones would allow the rays to be concentrated at the vertex. The dimensions of the patch formed would be roughly those of one given by a cylindrical canal-ray tube of diameter equal to the width of the gap. The increase of intensity would therefore be considerable; but the method is not easy to put into practice, and, in the case of deflexions through large angles, would necessitate a curved photographic surface.

Clearly the simplest way of increasing the intensity of the spot without increasing its dimensions, at any rate in one direction, is to use two parallel straight slits. In the case of the parabola method this device would only be of use in a special case such as the resolution of a close double, as the parabolas will only be sharp at points where they are parallel to the slit.

Such a slit system eliminates the difficulty of the penumbra mentioned above, at any rate so far as measurements at right angles to the line image are concerned.

**32. Possibilities of "focusing."**—Beams of charged particles which are homogeneous electrically (constant  $mv^2/e$ ) or magnetically (constant  $mv/e$ ) can be focused like rays of light by special devices.<sup>1</sup> The method of Dempster, described in the previous chapter, makes use of a form of magnetic focusing. But the rays generated by the ordinary discharge bulb are heterogeneous both in  $mv^2$  and  $mv$  so that what is required is an arrangement which will focus all rays of constant mass, even though their velocity may vary over an appreciable range.

**33. Principle of the mass spectrograph.**—This purpose is achieved by the arrangement illustrated diagrammatically in Fig. 8. The exact mathematical analysis has been worked out by R. H. Fowler,<sup>2</sup> but it is proposed to give only the approximate theory here for the sake of simplicity.

The rays after arriving at the cathode face pass through two very narrow parallel slits of special construction  $S_1$ ,  $S_2$ , and the resulting thin ribbon is spread out into an electric spectrum by means of the

<sup>1</sup> Aston, *Phil. Mag.*, 38, 709, 1919.

<sup>2</sup> Aston and Fowler, *ibid.*, 43, 514, 1922.

parallel plates  $P_1$ ,  $P_2$ . After emerging from the electric field the rays may be taken, to a first order of approximation, as radiating from a virtual source  $Z$  half-way through the field on the line  $S_1 S_2$ . A group of these rays is now selected by means of the diaphragm  $D$ , and allowed to pass between the parallel poles of a magnet. For simplicity the poles are taken as circular, the field between them uniform and of such sign as to bend the rays in the opposite direction to the foregoing electric field.

If  $\theta$  and  $\varphi$  be the angles (taken algebraically) through which the selected beam of rays is bent by passing through fields of strength  $X$  and  $H$ , then

$$\theta v^2 = lX \frac{e}{m} \quad (1), \text{ and } \varphi v = LH \frac{e}{m} \quad (2),$$

where  $l$ ,  $L$  are the lengths of the paths of the rays in the fields. Equation (1) is only true for small angles, but exact enough for practice.

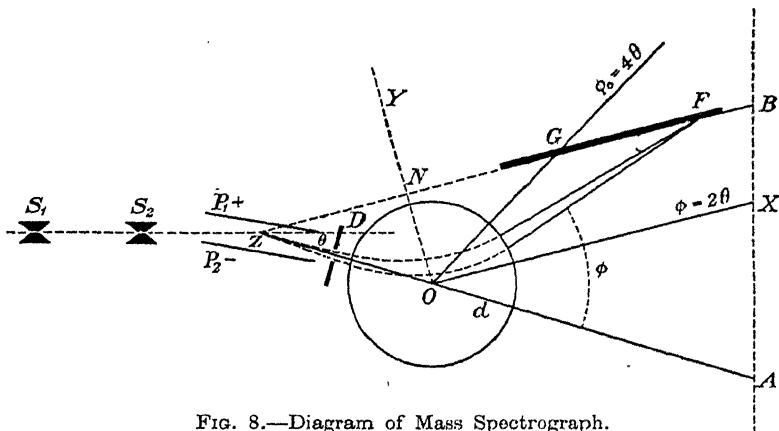


FIG. 8.—Diagram of Mass Spectrograph.

It follows that over the small range of  $\theta$  selected by the diaphragm  $\theta v^2$  and  $\varphi v$  are constant for all rays of given  $e/m$ , therefore

$$\frac{\delta\theta}{\theta} - \frac{2\delta v}{v} = 0, \text{ and } \frac{\delta\varphi}{\varphi} + \frac{\delta v}{v} = 0,$$

so that

$$\frac{\delta\theta}{\theta} = \frac{2\delta\varphi}{\varphi},$$

when the velocity varies in a group of rays of given  $e/m$ .

In order to illustrate in the simplest possible way how this relation may be used to obtain focusing, let us suppose the angles (exaggerated in the diagram) small and the magnetic field acting as if concentrated at the centre  $O$  of the pole-pieces. If the breadth  $ZO = b$ , the group

selected will be spread out to a breadth  $b\delta\theta$  at O, and at a further distance  $r$  the breadth will be

$$b\delta\theta + r(\delta\theta + \delta\varphi) \text{ or } \delta\theta \left[ b + r \left( 1 + \frac{\varphi}{2\theta} \right) \right] . \quad . \quad (3)$$

Now as the electric and magnetic deflexions are in opposite directions,  $\theta$  is a negative angle. Say  $\theta = -\theta'$ . Then if  $\varphi > 2\theta'$ , the quantity (3) will vanish at a value of  $r$  given by

$$r(\varphi - 2\theta') = b \cdot 2\theta'.$$

This equation appears correct within practical limits for large circular pole-pieces.

Referred to axes, OX, OY the focus is at  $r \cos(\varphi - 2\theta')$ ,  $r \sin(\varphi - 2\theta')$ , or  $r, b, 2\theta'$ ; so that to a first-order approximation, whatever the fields, so long as the position of the diaphragm is fixed, the foci will all lie on the straight line ZF drawn through Z parallel to OX. For purposes of construction G the image of Z in OY is a convenient reference point,  $\varphi$  being here equal to  $4\theta'$ . It is clear that a photographic plate, indicated by the thick line, will be in fair focus for values of  $e/m$  over a range large enough for accurate comparison of masses.

**34. Optical analogue.**—It may be a help to form an understanding of the principle of the apparatus if we suppose that the beam is one of white light and the electric and magnetic fields are glass prisms deflecting the light in opposite directions. The slit system acts as a collimator. If the glass of the first prism has a coefficient of dispersion double that of the second the heterogeneity of the rays of light will cause a spreading of the beam identical with that caused by heterogeneity (in respect to velocity) in the case of the positive rays. It will be clear that if we make the angle of refraction of the second prism more than double that of the first an achromatic image will appear at F.

Since it is a close analogue of the ordinary spectrograph and gives a "spectrum" depending upon mass alone the instrument is called a "mass spectrograph" and the spectrum it produces a "mass spectrum." It possesses one notable advantage over the optical spectrograph for, although we can never change the ratio of the dispersions, we can make the refractions whatever we will by the control of X and H, and so bring any desired range of the spectrum on to the plate.

**35. The discharge tube.**—Fig. 9 is a rough diagram of the original arrangement of the mass spectrograph when used for analysing positive rays generated by the ordinary discharge tube method. The discharge tube B is an ordinary X-ray bulb 20 cm. in diameter. The

anode A is of aluminium wire surrounded concentrically by an insulated aluminium tube to protect the glass walls, as in the Lodge valve.

The aluminium cathode C, 2·5 cm. wide, is concave, and placed just in the neck of the bulb—this shape and position having been adopted after a short preliminary research.<sup>1</sup> In order to protect the opposite end of the bulb, which would be immediately melted by the very concentrated beam of cathode rays, a silica bulb D is mounted

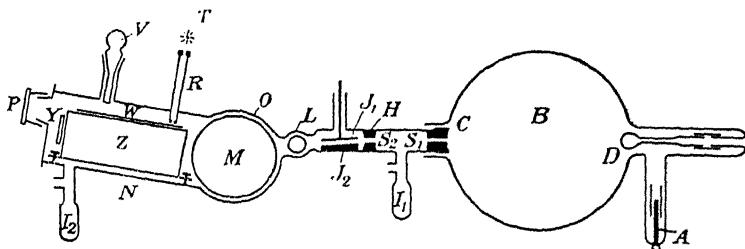


FIG. 9.—Diagram of the First Mass Spectrograph.

as indicated. The use of silica as an anticathode has the great advantage of cutting down the production of undesirable X-rays to a minimum. The cathode was earthed.

The discharge was maintained by means of a large induction-coil actuated by a mercury coal-gas break; about 100 to 150 watts were passed through the primary, and the bulb arranged to take from 0·5 to 1 milliampere at potentials ranging from 20,000 to 50,000 volts

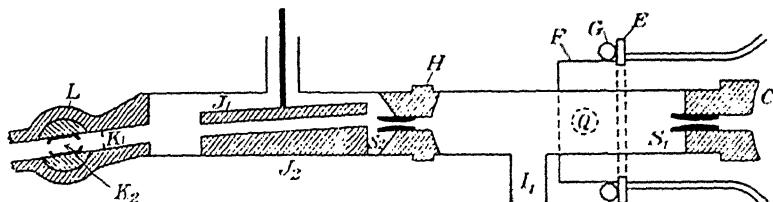
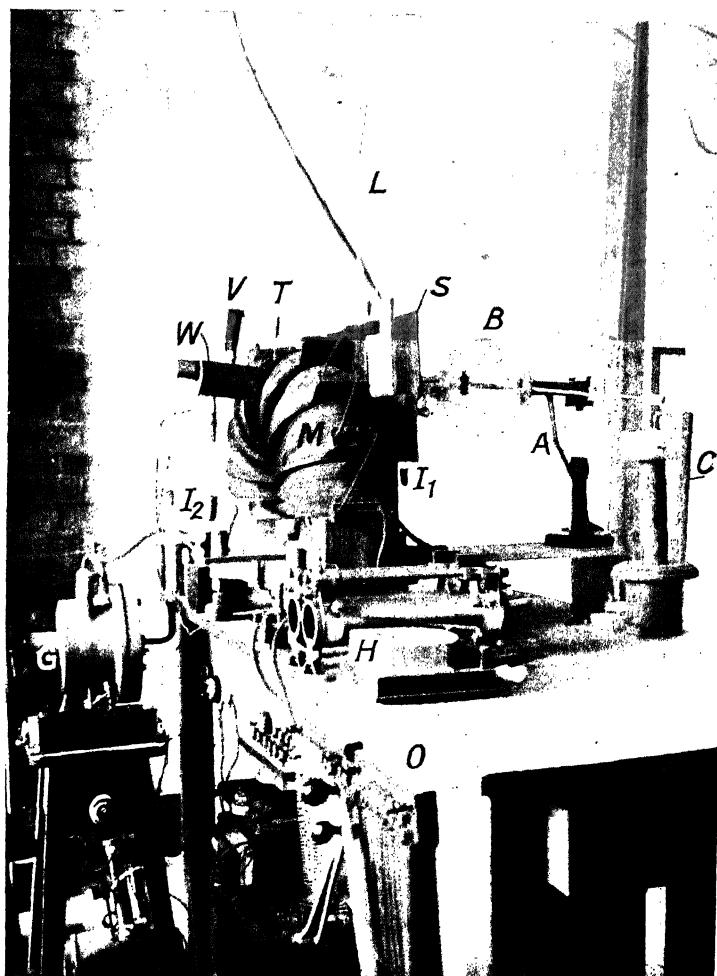


FIG. 10.—Mounting of Cathode of First Mass Spectrograph.

Owing to the particular shape and position of the electrodes, especially those of the anode, the bulb acts perfectly as its own rectifier.

The method of mounting the cathode will be readily seen from Fig. 10, which shows part of the apparatus in greater detail. The neck of the bulb is ground off short and cemented with wax to the flat brass collar E, which forms the mouth of an annular space between a wide outer tube F and the inner tube carrying the cathode. The concentric position of the neck is assured by three small ears of brass

<sup>1</sup> Aston, *Proc. Camb. Phil. Soc.*, 19, 317, 1919.



THE ORIGINAL MASS SPECTROGRAPH SET UP IN THE CAVENDISH LABORATORY IN 1919;  
NOW IN THE SCIENCE MUSEUM, SOUTH KENSINGTON.

B, Discharge Tube. A, Anode connected to high potential terminal of induction coil below table. C, Reservoir containing gas to be analysed. I<sub>1</sub>, I<sub>2</sub>, Charcoal-liquid air tubes exhausting slit-system and camera. S, Soft iron plates to shield discharge from stray magnetic field. L, Leads from high tension battery to electric plates. M, Du Bois electromagnet. T, Pea lamp for photographing fiducial spot. V, Vacuum-tight and light-tight control for moving photographic plate. W, Camera showing light-tight cap on the left. H, Magnet circuit ammeter. O, Magnet circuit control resistances. G, Gaede rotating mercury pump connected to the camera and the discharge tube by glass tubes and stopcocks.

it is therefore filled with hard paraffin to protect it from small particles of metal, etc., which if entering cannot be dislodged owing to its shape, and turned up taper to fit the standard mountings. After turning, the paraffin is easily removed by heat and solvents.

The position of the two slits is indicated in the diagram. They were roughly 0·05 mm. wide by 2 mm. long and could be accurately adjusted parallel to each other by means of their diffraction patterns. The space between them was exhausted by the liquid-air-cooled charcoal tube, I<sub>1</sub>.

**37. The electric field.**—The spreading of the heterogeneous ribbon of rays formed by the slits into an electric spectrum took place between two parallel flat brass surfaces, J<sub>1</sub>, J<sub>2</sub>, 5 cm. long, held 2·8 mm. apart by glass distance-pieces, the whole system being wedged immovably in the brass containing-tube in the position shown. The lower surface was earthed. The upper surface was raised to the desired potential, 200–500 volts, by means of a set of small storage-cells. In order to have the plates as near together as possible, they were sloped at 1 in 20—i.e. half the angle of slope of the mean ray of the part of the spectrum which is to be selected by the diaphragms. Of these there are two: one, K<sub>1</sub>, an oblong aperture in a clean brass plate, is fixed just in front of the second movable one, K<sub>2</sub>, which is mounted in the bore of a carefully ground stopcock L. The function of the first diaphragm is to prevent any possibility of charged rays striking the greasy surface of the plug of the stopcock when the latter is in any working position. The variable diaphragm is in effect two square apertures sliding past each other as the plug of the stopcock is turned, the fact that they are not in the same plane being irrelevant. When the stopcock is fully open as sketched in Fig. 10 the angle of rays passing is a maximum, and it may be stopped down to any desired extent by rotation of the plug, becoming zero before any greasy surface is exposed to the rays. Incidentally the stopcock serves another and very convenient use, which is to cut off the camera from the discharge tube, so that the latter need not be filled with air each time the former is opened to change the plate.

**38. The magnetic field.**—After leaving the diaphragms the rays passed between the pole-pieces M of a large Du Bois magnet of 2500 turns. The faces of these are circular, 8 cm. diameter, and held 3 mm. apart by brass distance-pieces. The cylindrical pole-pieces themselves are soldered into a brass tube O, which forms part of the camera N. When the latter is built into position, the pole-pieces are drawn by screwed bolts into the arms of the magnet, and so form a structure of great weight and rigidity and provide an admirable foundation for the whole apparatus. Current for, the magnet was provided by a special set of large accumulators. / With a potential of 300 volts on

the electric plates the hydrogen lines are brought on to the scale at about 0·2 ampere, and an increase to 5 amperes, which gives practical saturation, only just brings the singly-charged mercury lines into view. The discharge is protected from the stray field of the magnet by the usual soft iron plates, not shown.

**39. The camera.**—The main body of the camera N, which is exhausted by the charcoal tube I<sub>2</sub>, is made of stout brass tube 6·4 cm. diameter, shaped to fit on to the transverse tube O containing the pole-pieces. The construction of the plate-holder is indicated by the side view in Fig. 9 and an end-on view in Fig. 11. The rays, after being magnetically deflected, passed between two vertical earthed brass plates Z, Z about 3 mm. apart, and finally reached the photographic plate through a narrow slot 2 mm. wide, 11·8 cm. long, cut in the horizontal metal plate X, X. The three brass plates forming a T-shaped girder are adjusted and locked in position by a set of three levelling-screws, at each end; the right-hand upper one is omitted in Fig. 11. The plates Z, Z serve to protect the rays completely from any stray electric field, even that caused by the photographic plate itself becoming charged, until within a few millimetres of their point of impact.

The photographic plate W, which is a 2 cm. strip cut lengthwise from a 5 × 4 plate, is supported at its ends on two narrow transverse rails which raise it just clear of the plate X, X. Normally it lies to the right of the slot as indicated, and to make an exposure it is moved parallel to itself over the slot by means of a sort of double lazy-tongs carrying wire claws which bracket the ends of the plate as shown. This mechanism, which is not shown in detail, is operated by means of a torque rod V working through a ground glass joint. Y is a small willemite screen.

The adjustment of the plate-holder so that the sensitized surface should be at the best focal plane was done by taking a series of exposures of the bright hydrogen lines with different magnetic fields on a large plate placed in the empty camera at a small inclination to the vertical. On developing this, the actual track of the rays could be seen and the locus of points of maximum concentration determined. The final adjustment was made by trial and error and was exceedingly tedious, as air had to be admitted and a new plate inserted after each tentative small alteration of the levelling-screws.

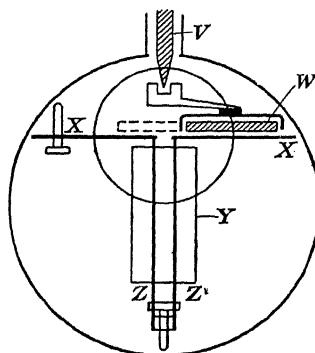


FIG. 11.—The Plateholder of the Camera.

**40. Experimental procedure.**—The plate having been dried in a high vacuum overnight, the whole apparatus was exhausted as completely as possible by the pump with the stopcock L open. I<sub>1</sub> and I<sub>2</sub> were then cut off from the pump by stopcocks and immersed in liquid air for an hour or so. The electric field, which ranged from 200 to 500 volts, was then applied and a small current passed through the magnet sufficient to bring the bright hydrogen molecule spot on to the willemite screen Y, where it could be inspected through the plate-glass back of the cap P. In the meantime the leak, pump, and coil, had all been started to get the bulb into the desired state.

When this was steady, J<sub>1</sub> was earthed, to prevent any rays reaching the camera, and the plate moved over the slot to its first position. The magnet current having been set to the particular value desired and the diaphragm adjusted, the coil was momentarily interrupted and J<sub>1</sub> raised to the desired potential, after which the exposure took place. During this, preferably both at the beginning and the end, light from a lamp T was admitted for a few seconds down the tube R (Fig. 9) the ends of which are pierced with two tiny circular holes. The lower hole is very close to the plate, so that a circular dot or fiducial spot is formed from which the measurements of the lines may be made.

The exposures ranged from 20 seconds in the case of hydrogen lines to 30 minutes or more, 15 minutes being usually enough. As soon as it was complete the above procedure was repeated, and the plate moved into the second position. In this way as many as six spectra could be taken on one plate, after which L was shut, I<sub>2</sub> warmed up, and air admitted to the camera. The cap P, which is on a ground joint, could now be removed, and the exposed plate seized and taken out with a special pair of forceps. A fresh plate was now immediately put in, P replaced and the camera again exhausted, in which state it was left till the next operation.

**41. Form of the spectrum lines.**—Owing to the form of the slits used, the shape of the spot formed when undeflected rays from such a slit system strike a photograph surface normally, is somewhat as indicated at *a* (Fig. 12). When they strike the plate obliquely the image would be spread out in one direction, as in *b*. This would be the actual form in the apparatus if the deflecting fields were unaffected by the passage of the rays. This appears to be the case in the magnetic field, but owing to an obscure polarizing effect<sup>1</sup> the electric field is weakened in the region of the beam, allowing rays of smaller energy to pass the diaphragm. As this effect is greatest in the centre this part of the beam will be more deflected by the magnet and the spot will take the form shown at *c*.

<sup>1</sup> V. p. 75.

The image on the plate will therefore be the part of this figure falling on the narrow slot in X, X; and as the apparatus is not exactly symmetrical, its shape in the spectra is the figure lying between the lines X, X in Fig. 12, c.

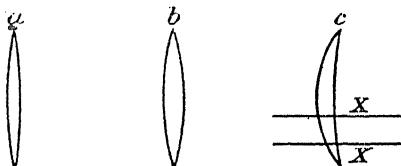


FIG. 12.—Form of the Spectrum Lines.

**42. The distribution of the mass spectrum over the photographic plate.**—In order to study the positions of the focus F (Fig. 8) on the plate corresponding to different values of the effective mass  $m$  when X and H are constant, we may assume perfect focusing and only consider a single median ray. If R is the radius of curvature of the path of a ray of effective mass  $m$  while in the magnetic field, and  $d$  the radius of the field, clearly  $\tan \frac{1}{2} \varphi = d/R$ . But X and  $\theta$  are constant, hence  $mv^2$  must be constant so that the radius of curvature in the magnetic field varies as  $\sqrt{m}$ . We may therefore write

$$\tan \frac{1}{2} \varphi = \sqrt{(m_0/m)} . . . . . \quad (4)$$

where  $m_0$  is a constant and can be interpreted as that mass which under the conditions of the experiment is bent through a right angle in the magnetic field.

Again if ON the length of the perpendicular dropped from the centre of the magnetic field upon ZF =  $p$  (a constant) then

$$NF = p \cot (\varphi - 2\theta) . . . . . \quad (5)$$

By combining (4) and (5) we get an expression for  $NF/p$  in terms of  $m_0$  and  $m$ . This is complicated,<sup>1</sup> but its differential can be shown to vanish when  $\tan \frac{1}{2} \varphi = \tan 2\theta$ . Thus the mass-scale is approximately linear near  $\varphi = 4\theta$ .

This linear law was observed experimentally at the very outset and though at the time it was unexplained it added greatly to the ease and accuracy of the determinations of  $m$ .

The quantity actually measured is the distance between a fixed point on the photographic plate called the "fiducial spot"<sup>2</sup> and the focused image F. Let us call this distance D. D and NF differ by a constant  $k$ —about 5.4 cm. in the apparatus—so that the relation between D and  $m$  has the form  $D = f(m/m_0)$  where  $f$  is a function in which all the coefficients  $p$ ,  $k$ , and  $\tan 2\theta$  are geometrical constants,

<sup>1</sup> Aston and Fowler, *Phil. Mag.*, 43, 515, 1922.

<sup>2</sup> V. p. 46.

the fields only affects  $m_0$ . It follows directly that so long as the apparatus is rigid :—If  $D_1$  and  $D_2$  are the distances from the fiducial spot of any two points on the plate and  $m_1$  and  $m_2$  the corresponding masses for given values of  $D_1$  and  $D_2$ , the ratio  $m_1/m_2$  will be the same in every photograph.

**43. Practical method of deducing the effective mass of a particle from the position of its line on the photograph.**—The mathematical investigation described above is of interest as it explains the results obtained, but the actual determination of masses from mass spectra was a purely empirical process, and consisted in the comparison of the positions of the lines caused by the masses in question with the positions of known reference lines. The only assumption made was that given at the end of the previous paragraph and even this was capable of verification by experiment, using such methods as that described below, or even more fundamentally, in the special case of the ratio 2/1, by the known identity of the mass ratios  $O_2/O$ ,  $O/O^{++}$ , and  $C/C^{++}$ .

The reference lines used at the outset of the work were lines given by particles of elements and compounds the relative masses of which were known to at least the order of accuracy aimed for. The procedure was somewhat as follows. A series of spectra were taken with say a mixture of  $CO_2$  and  $CH_4$  in the discharge tube. Previous experience with the parabola method of analysis led to the expectation that lines at 6— $C^{++}$ , 8— $O^{++}$ , 12— $C$ , 16— $O$ , 28— $CO$ , 32— $O_2$ , 44— $CO_2$  would certainly be present, there would also be a series of hydrocarbon lines between 12 and 16,  $CH$ ,  $CH_2$ ,  $CH_3$ , which could be regarded as known. A spectrum was selected containing as many as possible of these known lines and their masses  $m_1$ ,  $m_2$ ,  $m_3$ ,—were plotted against the distances of the lines from the fixed fiducial spot and a curve drawn through the points so obtained. This is our first *calibration curve*—of necessity inaccurate owing to the gaps between the points. A second spectrum was now taken in which the same lines appeared in a different place, for by altering the magnetic field we can place them wherever we please, and the new set of distances from the fiducial spot measured. These distances were now transformed into masses (no longer integral)  $m'_1$ ,  $m'_2$ ,  $m'_3$ ,—by means of the curve previously drawn. Supposing the curve to be accurate and the ratio law to hold  $\frac{m'_1}{m_1} = \frac{m'_2}{m_2} = \frac{m'_3}{m_3} = r$  where  $r$  is clearly a measure of the change in  $m_0$  in the mathematical discussion above. In practice these ratios were found to be very nearly the same, so that a mean value of  $r$  could be taken with confidence. The known masses multiplied by that mean now gave a new set of points on the original curve. By carrying

on this process all the serious gaps in the curve could be bridged and its accuracy brought up to the required standard.

The calibration curve so formed renders the identification of one line sufficient to deduce the masses corresponding to all the other lines on the plate, and as in general many lines are known on each spectrum, its accuracy is continually subject to fresh test. In practice it was found perfectly reliable so long as none of the geometrical constants of the apparatus were altered.

#### 44. Comparison of masses by the method of "coincidence."

—The method of deducing the masses of particles from the position of their lines described in the foregoing paragraph is simple and straightforward. It also has the great advantage of not requiring an accurate knowledge of the numerical values of the electric and magnetic fields. The only requisite is that these should be constant during the exposure and even if this constancy is not quite perfect the shift in position will affect all the lines known and unknown alike and therefore introduce no serious error into the results obtained. There is, however, another method of comparing masses which requires no knowledge, either theoretical or empirical, of the relation between effective mass and measured displacement. This is independent of the calibration curve and therefore constitutes a valuable check on results obtained by its use. It depends upon the following considerations: Suppose we wish to compare an unknown mass  $m'$  with a known mass  $m$ . A mass spectrum is taken with fields  $X$  and  $H$  such that the mass  $m$  gives a line at a certain position on the plate. The fields are now altered until the line caused by the unknown mass  $m'$  is brought to the identical position on the plate previously occupied by the line due to  $m$ . The paths of the rays in the two cases must be identical, hence if  $X'$ ,  $H'$  are the new values of the fields it follows at once from equations (1) and (2)<sup>1</sup> that  $m'/m = X/X' \times (H'/H)^2$ . Now it is only necessary to measure one of the fields if we keep the other constant and therefore  $H$ , which cannot be measured or reproduced accurately, was kept constant and  $X$  was assumed to be proportional to the potential applied to the plates  $P_1 P_2$ . Thus the position occupied by the line 12 due to carbon with a potential on the plates of 320 volts should be exactly coincident with that occupied by line 16 due to oxygen with 240 volts, when the magnetic field was held constant. All such coincidences were found to occur to the accuracy then attainable.

Methods depending on the measured variation of  $X$  with  $H$  constant have some practical disadvantages. The first and most obvious of these is that any small change in the value of the magnetic field between the two exposures will lead to a definite error, this error will

<sup>1</sup> V. p. 40.

be double the percentage change in the field, since the square of the latter is involved. The second objection is founded on considerations of intensity. If the parabola method of analysis is compared with the mass spectrograph it will readily be observed that, in effect, the latter focuses at a point all the rays which in the former method form a short element of arc on a parabola. The length of the element of arc is determined by the angle of the electric spectrum allowed to pass, i.e. the width of the diaphragm. Its position on the parabola is at our disposal, for, referring to Fig. 4, p. 26, it will be seen that the higher we make  $X$ , that is to say the higher the energy of the beam of rays we select at constant  $\theta$ , the nearer the element of arc will approach the axis OY, in fact its distance from that axis will simply be inversely proportional to  $X$ . Also, however many parabolas we consider and however much we move them about by changing H, so long as X is constant the elements of arc selected will all lie on a line parallel to OY. Now it has already been pointed out<sup>1</sup> that the intensity of normal parabolas is a maximum near the head  $p$ , where the energy corresponds to the full fall of potential across the discharge tube, and fades away rapidly, in some cases very rapidly indeed, at points more distant from the origin. In order to get the greatest intensity at the focused spot we must therefore choose X so that the element of arc selected will be near the head of the parabola. This is done in practice by observing visually, by means of a willemite screen, the very bright line given by the hydrogen molecule while different potentials are applied to the plates. The best value of X so determined must also be the best value for all the other normal lines, so that in the ordinary calibration curve method, when X is kept constant, it is possible to use conditions in which all the normal lines on the mass spectra will be at their brightest together, whatever range we bring on to the plate by altering the magnetic field.

In the coincidence method this very fortunate circumstance cannot be taken advantage of, for with H constant the selected elements of arc will now lie on a line parallel to OX. We can only arrange matters for one, the lighter, of the two masses to be compared, to be at its optimum. In the case of the heavier the selected arc must lie at a greater distance from the origin and therefore provide a much feebler intensity. The disparity in brightness, due to this effect, will be the greater the greater the ratio of the masses considered; it can be corrected to some degree by softening the discharge tube while the heavier mass is being photographed.

In spite of these drawbacks the principle of the method of coincidences has been the underlying one in the development of methods

<sup>1</sup> V. p. 27.

of precision. Its first notable application was in the measurements of the masses of helium and hydrogen.<sup>1</sup>

**45. The determination of the masses of atoms of hydrogen and helium by the method of "bracketing."**—The determination of masses so far removed as these from the ordinary reference lines offers peculiar difficulties, but, as the lines were expected to approximate to the terms of the geometrical progression 1, 2, 4, 8, etc., the higher terms of which are known, a special method was adopted by which a two to one relation could be tested with some exactness. Two sets of accumulators were selected, each giving very nearly the same potential of about 250 volts. The potentials were then made exactly equal by means of a subsidiary cell and a current-divider, the equality being tested to well within 1 in 1000 by means of a null instrument. If exposures are made with such potentials applied to the electric plates first in parallel and then in series, then magnetic field being kept constant, all masses having an exact two to one relation will be brought into coincidence on the plate.<sup>2</sup> Such coincidences cannot be detected on the same spectrum photographically; but if we first add and then subtract a small potential from one of the large potentials, two lines will be obtained which closely bracket the third. To take an actual instance—using a gas containing hydrogen and helium, with a constant current in the magnet of 0.2 ampere, three exposures were made with electric fields of 250, 500 + 12, and 500 - 12 volts respectively. The hydrogen molecule line was found symmetrically bracketed by a pair of atomic lines (Plate III, Spectrum VII, *a* and *c*), showing within experimental error that the mass of the molecule is exactly double the mass of the atom. When after a suitable increase of the magnetic field the same procedure was applied to the helium line and that of the hydrogen molecule, the bracket was no longer symmetrical (Spectrum VII, *b*), nor was it when the hydrogen molecule was bracketed by two helium lines (*d*). Both results show in an unmistakable manner that the mass of He is less than twice that of H<sub>2</sub>. In the same way He was compared with O<sup>++</sup>, and H<sub>3</sub>.<sup>3</sup> The method is discussed on p. 49. The values obtained by its use can be checked in the ordinary way by comparing He with C<sup>++</sup> and H<sub>3</sub> with He, these pairs being close enough together for the purpose. Table II gives the range of values obtained from the most reliable plates.

These figures led to the conclusion that hydrogen was a simple element and that the mass of its atom corresponded to the chemical atomic weight and was definitely divergent from a whole number,

<sup>1</sup> Aston, *Phil. Mag.*, 39, 611, 1920.

<sup>2</sup> V. p. 48.

<sup>3</sup> V. p. 118.

TABLE II

Line.	Method.	Mass assumed.	Mass deduced.
He . . . . .	Bracket	O++ = 8	3.994-3.996
	Direct	C++ = 6	4.005-4.010
H <sub>3</sub> . . . . .	Bracket	C++ = 6	3.025-3.027
	Direct	He = 4	3.021-3.030
H <sub>2</sub> . . . . .	Bracket	He = 4	2.012-2.018

a result of fundamental importance.<sup>1</sup> Incidentally they furnished conclusive proof that the body of mass 3 first observed and investigated by Sir J. J. Thomson<sup>2</sup> was actually a molecule consisting of three hydrogen atoms, a result independently established about the same time by the chemical work of Wendt and Landauer.<sup>3</sup>

**46. The measurement of the lines.**—The accurate determination of the distance of the lines from the fiducial spot is a physical problem of considerable interest. The image itself is due to a caustic of rays, the edge of which will be sharp on the side of maximum magnetic displacement, so that this, the left side in the plates, may be expected to maintain its sharpness when a large diaphragm is in use, while the other will fade away gradually. Hence very bright lines will be broadened to the right by this effect (which is analogous to spherical astigmatism in ordinary lenses), but to the left the only broadening will be that due to ordinary halation. The relative importance of these two forms of spreading can be gauged by taking photographs with a very small diaphragm, for then the first will be eliminated and the second can be estimated by comparing lines of different intensity. It is found that for ordinary diaphragm apertures the halation effect is much the smaller; it can also be minimized by using lines of approximately equal intensity so that the most reliable measurements of lines for position are obtained from their left-hand edges. This is well illustrated in the "bracketed" lines of hydrogen *a* and *c*, Plate III. In (*a*) measurements of the left-hand side of the three lines shows this bracket to be really symmetrical though it does not appear so to the eye, on account of the astigmatic spreading of the middle line caused by the use of an open diaphragm and rather too long an exposure. In (*c*) the diaphragm was almost closed and the exposures more carefully adjusted, so that both sides of the lines are sharp and their breadths practically identical.

The most accurate measurements were made on a comparator.

<sup>1</sup> V. p. 199.

<sup>2</sup> J. J. Thomson, *Rays of Positive Electricity*, p. 116, 1913.

<sup>3</sup> Wendt and Landauer, *J. Amer. Chem. Soc.*, **42**, 930, 1920.

The spectrum was set as closely as possible parallel to the axis of the instrument, and the distances between the left-hand edge of the lines and the fiducial spot read off on a Zeiss standard scale. For faint lines it was necessary to use a very low power eyepiece of the reading microscope, and in the case of the faintest lines of all, the best results could be obtained by laying a millimetre scale on the plate and estimating the distance from the fiducial spot to the optical centre of the lines, by the unaided eye.

**47. Resolving power and accuracy of mass determination.**—Taking the width of the slits as 1/25 mm. and putting in the dimensions of the apparatus the theory shows that in the region  $\varphi = 4\theta$  lines differing by a little less than 1 per cent. should be just separated. In actual practice a better result was obtained, for the instrument proved capable of separating the lines of xenon, which differ by 1 in 130; this is probably because the part of the line which falls on the strip of plate exposed is due to the narrower edges of the slits.

The numerical relation between mass and position in this part of the spectrum corresponds to a shift of 1.39 mm. for a change of mass of 1 per cent., so that even with the unaided eye an accuracy of 1 part in 1000 could be approached. Although it is sufficient in theory to know the mass of one line only to determine, with the calibration curve, the masses of all the others, in practice every effort was made to bracket any unknown line by reference lines and only to trust comparative measurements when the lines are fairly close together. Under these conditions an accuracy of 1 in 1000 was attainable.

**48. Lines of the first, second and higher orders.**—It was shown on page 28 that particles having two charges gave a parabola corresponding to an effective mass of one-half the normal mass. In the same way a particle with three charges will have an effective mass of one-third, and so on. These apparent masses will duly make their appearance on mass spectra as lines corresponding to simple fractions of the real mass causing them. It is convenient in these cases to borrow the nomenclature of optics and refer to the lines given by singly, doubly, and multiply charged particles respectively as lines of the first, second, and higher orders. Thus the molecule of oxygen gives a first-order line at 32, and its atom first- and second-order lines at 16 and 8.

**49. Molecular lines of the second order.**—The work of Sir J. J. Thomson on multiply charged positive rays showed very definitely that molecules carrying more than one charge were at least exceedingly rare,<sup>1</sup> for not a single case was observed which could not be

<sup>1</sup> J. J. Thomson, *Rays of Positive Electricity*, p. 54.

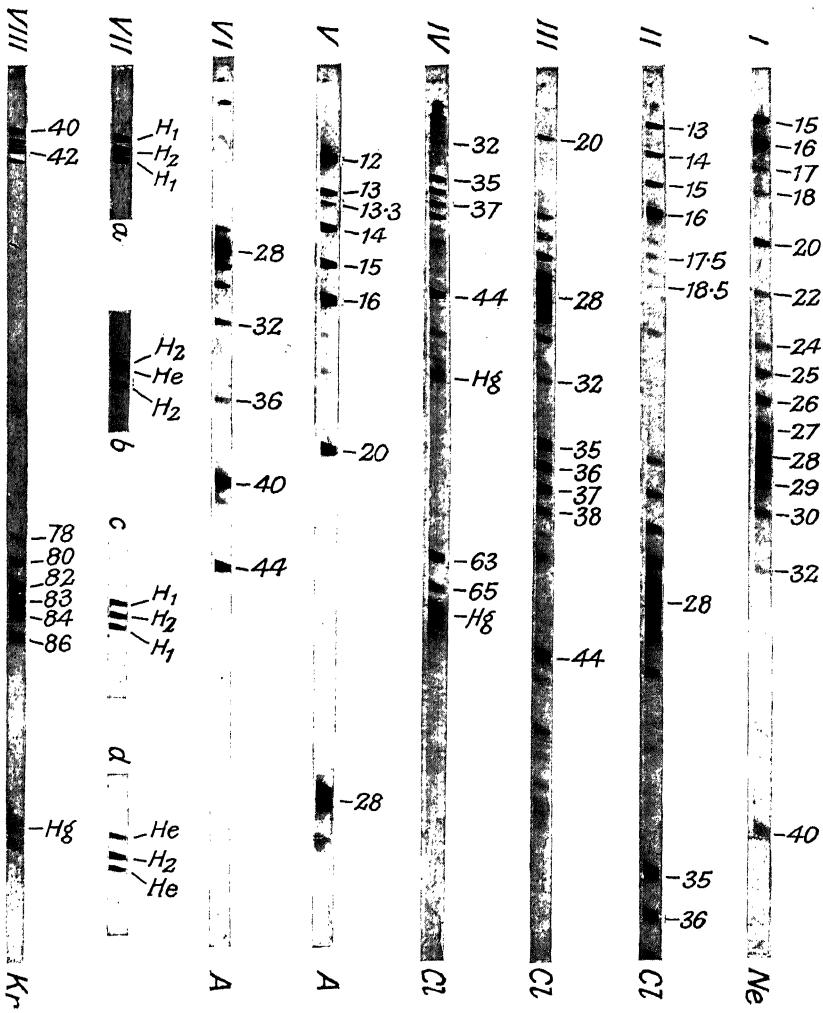
explained on other grounds. Up to the time of the experiments with the fluorine compounds the same could be said of the results with the mass spectrograph. This absence of multiply charged molecular lines, though there is no particular theoretical reason for it, was used as confirmatory evidence on the elementary nature of doubtful lines.

The spectra obtained with  $\text{BF}_3$  show lines for which there appears no possibility of explanation except that of doubly charged compound molecules. The two most obvious of these may be seen on Plate IV, Spectrum III, and at the extreme left-hand end of Spectrum IV. They correspond to masses 23.50 and 24.50, the first being quite a strong line. Were there no lines of lower order corresponding to these, the whole-number rule might be in question; but all doubt is removed by the fact that the lines 47 and 49 are two of the strongest on the plate. A comparison of several spectra upon which these lines occur shows a definite intensity relation which practically confirms the conclusion that the first pair of lines are true second-order lines corresponding to the first-order lines of the second pair. Now lines 47 and 49 cannot by any reasonable argument be elementary, they must in fact be due to compounds of fluorine.

**50. Negative mass spectra.**—It has been mentioned that positive rays could become negatively charged by the capture of electrons by collisions in the narrow canal-ray tube of the Thomson apparatus,, and so produce parabolas in the quadrant opposite to that containing the normal ones. The slit system of the mass spectrograph is specially designed to eliminate such collisions as far as possible by exhausting the space between the slits. If the means of exhaustion of this space is deliberately cut off, and the normal electric and magnetic fields both reversed in sign it is possible, at a small cost in definition of the lines, to photograph the mass spectra of negatively charged particles. Such negatively charged particles are only formed by elements or compounds having marked electronegative properties.

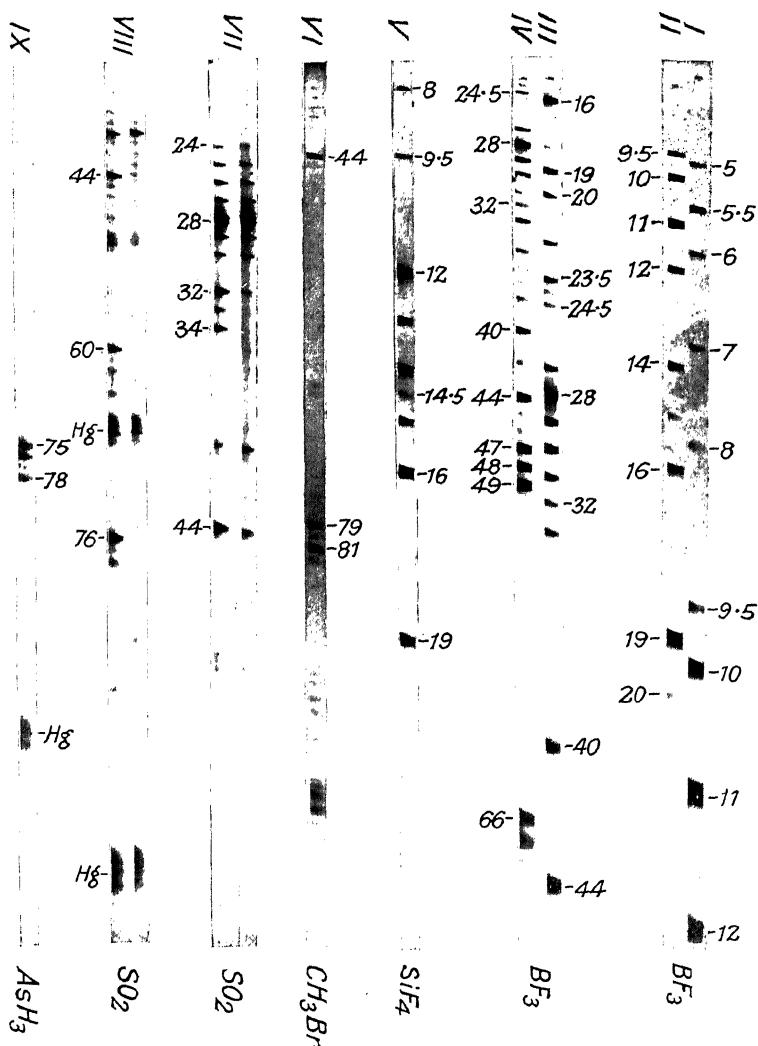
**51. Mass numbers and isotopic weights.**—The problem of nomenclature of the isotopes became serious when the complex nature of the elements generally became apparent. The plan used by the writer, which was generally adopted, is to qualify the ordinary chemical symbol of the complex element with an index corresponding to the mass of the individual isotope. This index is called the "mass number" of the atom. At first the index was put on the right of the symbol, e.g.  $\text{Ne}^{22}$ , but later the International Committee on nomenclature recommended that it should be placed on the left, e.g.  $^{23}\text{Na}$ . This ruling is now generally accepted in Europe, and will be adopted in this book. On the other hand American writers still use the older plan, a typical example of the difficulties with which inter-

PLATE III



ATYPICAL MASS SPECTRA OBTAINED WITH THE FIRST MASS SPECTROGRAPH, 1920.

PLATE IV



## TYPICAL MASS SPECTRA OBTAINED WITH THE FIRST MASS SPECTROGRAPH, 1920.

national advisory bodies have to contend. When there can be no possible misunderstanding as to which isotope is concerned the index, for convenience, may be omitted.

The actual mass of the neutral atom of an individual isotope is now called its "Isotopic Weight" and is expressed on the Physical Scale  $^{16}\text{O} = 16$ .<sup>1</sup>

**52. Results obtained with the first mass spectrograph.**—The original instrument, adapted from time to time to suit particular needs, was in continual use from 1919 till it was dismantled in 1925, with results which will be given in Part III. Typical spectra obtained by its means are reproduced in Plates III and IV. The first experiments were done on neon and the spectra obtained gave the first entirely satisfactory proof that this consisted of isotopes each of whole number mass.<sup>2</sup> As the work progressed with chlorine and other complex elements it soon became clear that all atoms had masses which were integrally related to a close approximation, the "whole number rule." Hydrogen, as theoretically expected, was found to be an exception to this. Indications were obtained that other elements such as lithium and iron would show similar but smaller variations, but the measurement of these required more powerful instruments and methods the development of which will now be described.

<sup>1</sup> V. p. 198.

<sup>2</sup> Aston, *Phil. Mag.*, **39**, 449, 1920.

PART II  
PRODUCTION AND ANALYSIS OF MASS SPECTRA  
CHAPTER VI  
TECHNIQUE OF GAS DISCHARGE

**53. Objects to be attained.**—As in optical spectra, advance in the analysis of mass spectra is definitely limited by the intensity of the source of rays. It is useless to design apparatus of higher resolving power unless the intensity of illumination of the image-forming slit is increased to correspond. The most convenient and controllable source of intense beams of mass rays is the discharge in a gas at low pressure. As has already been stated, our knowledge of the mechanism of this is still incomplete and largely empirical. To take advantage of the fact that the slit to be illuminated is usually extremely small it has always been the writer's aim to devise forms of discharge which give beams of rays sharply concentrated rather than of great total intensity. Other things being the same, the latter can always be obtained by forcing more current through the discharge, but beyond a certain point this soon defeats its object by limiting the duration of the exposure and in many other ways.

**54. Cylindrical discharge tubes.**—In all the very early work on canal rays by Goldstein, J. J. Thomson, Wien and others, cylindrical discharge tubes were used, and for many types of research they are undoubtedly the most effective. The concentration of the positive stream towards the centre of the cathode is very marked as the negative glow retreats under reduced pressure. This concentration, which is indicated in Fig. 13, conveniently limits the working area of the cathode so that a gap can be left between it and the walls allowing gas to be introduced or pumped off at cathode (generally earth) potential. At the same time it automatically focuses the beam towards the centre where the slit is placed.

At first sight it would appear that by accurate lining up of the tube and proper reduction of pressure a solid beam of rays of indefinitely high intensity could be focussed on the geometrical centre of the cathode travelling in the direction of the axis of the tube. Un-

fortunately in practice it is found that beams focused in this way resemble hollow cones rather than solid rods, so that with a very fine slit it is the accidental coincidence of this with the edge rather than with the middle of the cone which is effective. Since the position of these areas of high concentration seems to depend on minute alterations of the geometry of the tube and cathode, the element of chance is always present, but once a good setting has been obtained

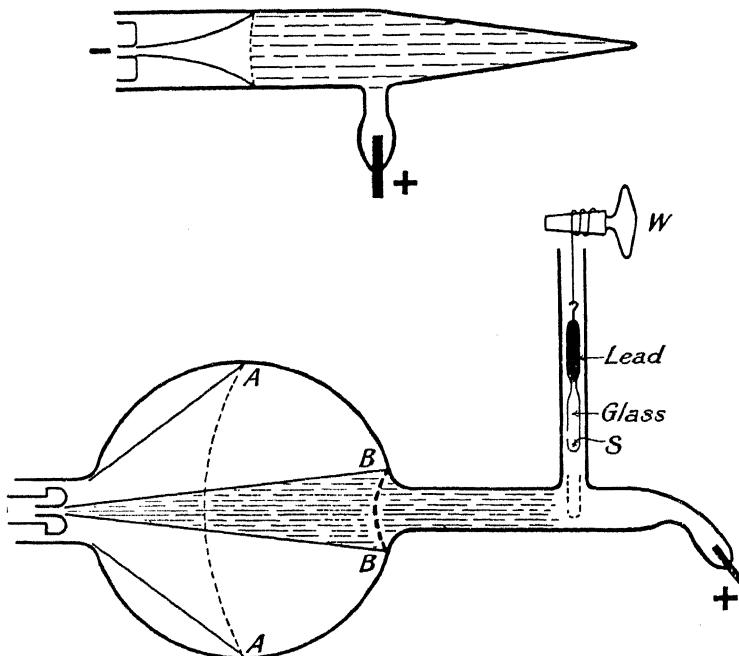


FIG. 13.—Cylindrical and Spherical Discharge Tubes (for the production of mass rays).

it will usually last for a considerable time. The anode may be located anywhere beyond the dark space. In order to dissipate the energy of the cathode rays the simplest plan is to draw off the end of the tube into a long taper, as shown in the figure.

**55. Spherical discharge tubes.**—For practically the whole of the writer's work on mass spectra obtained by gas discharge large spherical "bulb" discharge tubes were employed. The form at present adopted after many years' experience is shown in Fig. 13. The bulb is 8 in. in diameter—6-in. bulbs have also been used—with a neck 1·5 in. internal diameter containing the cathode. This is a solid hemisphere of aluminium 1 in. in diameter drilled with a hole of about 3 millimetres and turned to the toroid section indicated by

rounding off the edges. This form, although it is slightly less efficient, is preferred to the concave type used with the first mass spectrograph because it appears to be less acutely sensitive to change in position and does not necessitate a special anticathode to dissipate the energy of the cathode rays. These are given off from a cathode of this form in two groups, a diffuse wide cone striking the walls as far back as the circle A, A, and a much more concentrated beam emerging from the cathode pit as the cone B. B, the energy of which is dissipated in the long neck tapered and terminating in the anode as shown. With this arrangement 1 milliampere at 40 kilovolts can be used for an indefinite period without any artificial cooling of the glass walls being required.

The best position for the cathode in the neck is roughly as shown, but has to be found by trial for any fresh setting of the apparatus. The concentration of the beam of mass rays into the cathode pit appears to be produced in a similar manner, but at much lower pressures, to that in the cylindrical form and is extremely sensitive to change in geometry. The shift sideways of the neck with respect to the cathode of a fraction of a millimetre may make all the difference between success and failure so that a good setting cannot always be produced after the bulb has been dismounted. On the other hand, once obtained a favourable setting can be used continually until the walls of the neck become coated with aluminium sputtered from the cathode or other products of decomposition. This coating may be cleaned off with weak hydrofluoric acid solution and the bulb used again.

**56. Introduction of the sample into the discharge.**—In the case of gases or materials having high vapour pressures admission to the discharge is made continuously through a fine glass leak. The rate is controlled by pressure in the reservoir and balanced by pumping to give the desired hardness to the discharge. The inlet and outlet tubes should be behind the cathode where the gas is not at high potential. Compounds such as uranium fluoride or osmium tetroxide having vapour pressures too low for a fine leak may be admitted through a small stopcock either continually, the rate being controlled by temperature adjustment, or in doses. If the boiling-point is too high for this a special vertical winch arrangement must be attached as indicated (Fig. 13). The solid is placed in a glass bucket and lowered by means of the winch W into the anode neck where it is vaporized by the heat of the cathode ray stream. This method has been successfully employed for selenium and rhenium heptoxide. Bainbridge used cavities drilled in the cathode itself to contain the substances, such as tellurium, which were to be vaporized, and Mattauch has applied this device to compounds of the rare earths.

**57. Relative merits of cylinders and bulbs.**—This question has been the subject of a good deal of controversy and the answer really depends on the particular class of work for which the rays are required. The bulb type was introduced by the writer during the early work on positive rays in the Cavendish Laboratory because it enabled the discharge to pass at the lowest pressures. This was of the first importance at a time when large "canal" tubes were used and no means, or only inadequate means, were available for reducing the pressure in the camera below that of the discharge. Nowadays the use of extremely fine apertures and improved means of maintaining high vacua have removed some of the objections to the higher discharge pressure in cylinders, and Wien claims that these are overwhelmingly superior to bulbs when the total quantity of rays passing through the small aperture at the centre of the cathode is measured. The writer's experience agrees with this as far as total quantity, as opposed to constitution, of the rays is concerned. The bulb is in general inferior to the cylinder in this respect, but if sufficient pains are taken to get the cathode into the best position its inferiority is not nearly so marked as the figures published by Döpel<sup>1</sup> would suggest. The cylindrical tube is easier to make and to fit. It can be exhausted much quicker and is therefore particularly suitable for preliminary testing. It was used in this way in connection with the second mass spectrograph and proved of the greatest value in providing bright hydrogen lines for visual observation on the willemite screen. On the other hand, the rays produced in a cylindrical discharge tube have their energies concentrated into a very much smaller range than those of a bulb. This, though advantageous in some cases, is entirely unsuitable for measurements of mass of high precision which depend on the comparison of particles with energies differing by a ratio as high as 2 to 1. Furthermore, the low-pressure discharge in the bulb appears to be much more favourable to the formation of those multiply charged particles which are necessary to establish and check accurate ratios of mass.

**58. Peculiarities of gas discharge.**—After over thirty-five years' experience with vacuum discharges the writer knows no method of obtaining, still less of reproducing, first-class results with any certainty. Although our knowledge has advanced enormously in that period<sup>2</sup> there are still many gaps, and the extreme complexity of the mechanism of this form of discharge renders its use much of an art rather than a science. Both its phenomena and its limitations abound in the curious and unexpected.

<sup>1</sup> Döpel, *Ann. der. Physik.*, **4**, 23, 1925.

<sup>2</sup> V. *Rev. Mod. Phys.*, **2**, 123, 1930; **12**, 87, 1940.

There is, for instance, the fact that though it gives highly satisfactory results with potentials of 10 to 60 kilovolts above the latter ever-increasing experimental difficulties develop. The discharge becomes impracticable and to obtain positive rays of 100 kilovolts or over, such as are required for artificial disintegration, supplementary high vacuum accelerating fields must be used. Thus in the well-known experiments of Cockcroft and Walton<sup>1</sup> the protons were generated in a cylindrical tube with a toroid cathode at a low voltage and then passed through suitable accelerating fields to raise their energy to the value required.

The inert gases must always be diluted with some other gas such as carbon dioxide, otherwise they cause excessive sputtering of the cathode. It may be taken as a general rule that pure materials do not behave well in the gas discharge and tend to make it unsteady. The presence of heavy ions such as mercury usually steady the discharge. It has long been known that the introduction of a heavy inert gas may be beneficial.<sup>2</sup> On the other hand, the presence of elements of low ionization potential such as mercury may suppress the production of mass ray of others entirely. Thus all the early attempts to produce the mass spectrum of zinc from the discharge in zinc methyl failed completely and it was only by using the vapour in the absence of mercury that success was achieved. An excellent example of the extraordinarily uncertain nature of this type of research is afforded by the analysis of rhenium heptoxide.<sup>3</sup> In order to supply the enormously intense beams of protons and deuterons now used in high voltage disintegration apparatus Oliphant<sup>4</sup> designed a form of discharge tube made of steel tubing. This can deal with discharges of 10 to 100 milliamperes at 20 kilovolts. The energy of the cathode rays is dissipated by an oil cooled anticathode while the cathode itself may be run at a red heat. An alternative intense source of hydrogen ions is the low voltage arc described by Tuve, Dahl and Hafstad.<sup>5</sup>

**59. Effects of compounds in the discharge.**—Locked at purely as a means of discovering and identifying isotopes the gaseous discharge has the defect that it produces a wealth of molecular lines in addition to the atomic ones required, and although in exceptional cases these afford valuable confirmation, in general they merely confuse the evidence and render its interpretation more difficult. In the first place allowance must always be made for the presence of compounds of hydrogen, carbon, oxygen and silicon derived from the

<sup>1</sup> Cockcroft and Walton, *Proc. Roy. Soc., A*, **136**, 619, 1932.

<sup>2</sup> Aston, *ibid.*, **A**, 103, 468, 1923.

<sup>3</sup> V. p. 178.

<sup>4</sup> *Proc. Roy. Soc., A*, **141**, 259, 1933.

<sup>5</sup> *Phys. Rev.*, **48**, 241, 1935.

walls of the discharge tube. There is little doubt that the faint isotopes of oxygen 17 and 18 would have been discovered on the mass spectra of that element had there been any means of guaranteeing that effects produced at these positions were not due to OH and OH<sub>2</sub>.

In combining with an element to give lines which may be mistaken for its isotopes hydrogen is obviously the only serious culprit. In the early days all faint lines immediately following strong ones were regarded with the greatest suspicion. The lines 33 and 34 (Spectrum VII, Plate IV) were taken to be hydrides of sulphur and another at 21 to be an abnormal hydride of neon. When later it was found that these actually were true isotopes these precautions were relaxed to a certain extent with the unfortunate result that lines 65 and 69 in the mass spectrum of zinc obtained by the discharge through its methyl were erroneously ascribed to true isotopes. Other misleading effects of this kind will be noted in Part III under the elements concerned.

**60. Bands in mass spectra.**—Attention has already been called to effects produced in the parabola method of analysis by collisions made by the rays in the camera itself and called by Sir J. J. Thomson “secondary rays.”<sup>1</sup> The particular arrangement of opposed fields in the mass spectrograph virtually prevents effects of this kind by reducing them in general to a faint continuous background on the mass spectra produced. If, however, very intense molecular beams are in use and the vacuum in the camera is allowed to deteriorate, interesting secondary phenomena may be observed. One of these effects was first noticed while the second mass spectrograph was in process of construction. On this occasion very wide slits, with resulting poor vacuum in the camera, were being used for testing, and a distinct broad band was observed on the willemite screen in the region corresponding to a mass of half a unit.

Some years later during the preliminary running in of a new discharge bulb, which always results in abnormally strong beams of rays, a similar band effect was noticed on a photographed mass spectrum, this time in the region 5·2. The matter was further investigated and the band in region 0·5 was again observed and this time photographed. It was found that the positions of the bands on the mass scale were not affected by the alteration of the fields. Fig. 14 shows the photometric observations on the bands which show their centres to be 0·515 and 5·18 respectively. A special subsidiary electric deflecting field was now attached to the camera and by observations with this it was demonstrated beyond any doubt that the particles causing the lighter band were protons, that is to say singly charged

<sup>1</sup> V. p. 27.

hydrogen atoms, with half normal energy. The presence of this type of secondary ray had already been suggested by the beading on the hydrogen parabolas<sup>1</sup> and the explanation then suggested is doubtless correct.

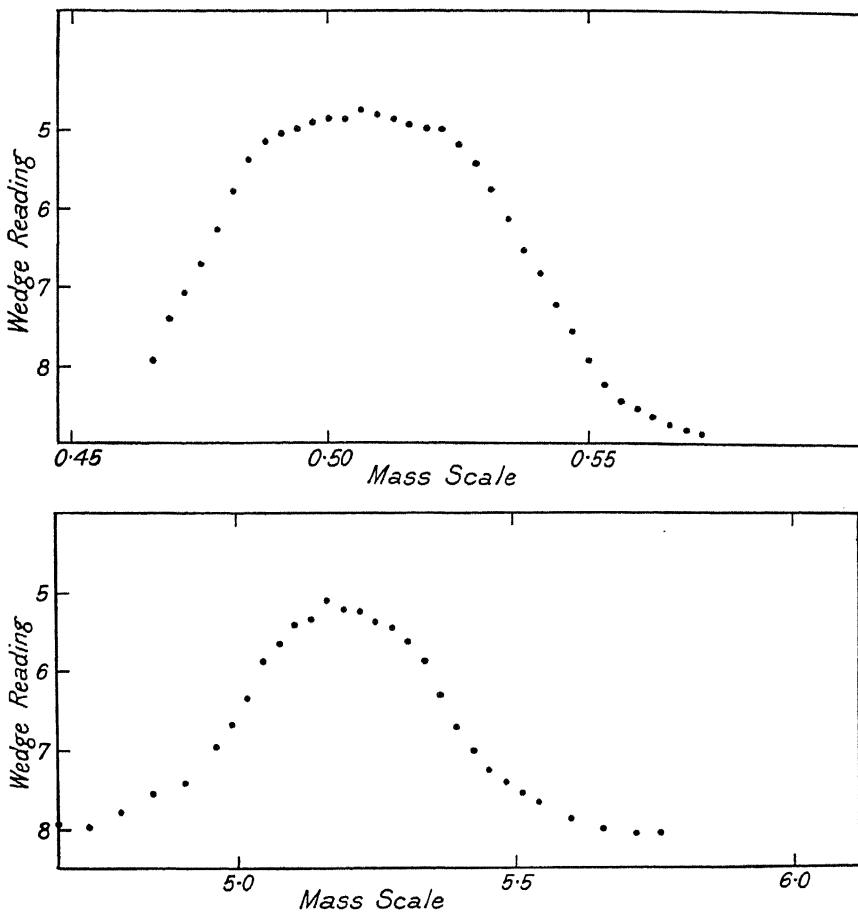


FIG. 14.—Bands in Mass Spectra.

The two bands are associated with the presence of two quite abnormally bright molecular lines due to the hydrogen molecule and the carbon monoxide molecule respectively. If a normal singly charged  $H_2$  molecule is dissociated after it leaves the electric field and one of the atoms formed retains the positive charge through the magnetic field it will simulate a normal primary ray of mass 0.5. If we suppose

<sup>1</sup> Aston, *Proc. Camb. Phil. Soc.*, **19**, 317, 1920.

that the dissociations are caused by collisions, the particles will have impressed upon them a random change in velocity and direction and so tend to form a band and not a line.

Turning now to the case of the CO molecule here the atoms composing it have masses in the ratio 3 to 4 so that if the carbon atom retains the positive charge after the dissociation it will simulate a mass  $3/7 \times 12$ , that is 5.14. This is clearly the cause of the band observed. No effect could be seen at mass  $4/7 \times 16$  which leads to the very interesting conclusion that when  $\text{CO}^+$  is dissociated the positive charge remains with the atom of carbon rather than that of oxygen.

An account of these bands and their explanation was given at the meeting of the British Association in 1930. Seven years later Bainbridge and Jordan<sup>1</sup> observed the one at mass  $5\frac{1}{7}$  in spectra obtained with their double focusing instrument<sup>2</sup> and estimated its position on the mass scale by comparison with lines  $\text{D}_2\text{H}$  and  $^{16}\text{O}^{++}$ . This was  $5.145 \pm 0.002$  in exact agreement with theory.

Quite recently the subject has been very fully investigated, and most beautiful photographs of dissociation bands published by Mattauch and Lichtblau.<sup>3</sup> Their type of double focusing mass spectrograph<sup>4</sup> gives very narrow bands and they describe no less than 28 different ones, together with the processes of molecular dissociation which give rise to them.

<sup>1</sup> *Phys. Rev.*, **51**, 595, 1937.

<sup>2</sup> V. p. 111.

<sup>3</sup> *Phys. Zeit.*, **40**, 16, 1939.

<sup>4</sup> V. p. 113.

## CHAPTER VII

### ANODE RAYS

**61. Mass rays of metallic elements.**—The use of the ordinary gas discharge described in the previous chapter is clearly limited to those elements which may be introduced as vapours or vaporizable compounds into the discharge itself. A large number, including the majority of the metallic elements, are unsuitable for this treatment so that other devices had to be employed to produce their mass rays. Although in a few cases, such as that of magnesium, the first analyses were performed with rays produced by direct ionization of the vapour, a more generally effective method was the employment of a special discharge from an anode which itself produces the rays required.

Such an anode was originally discovered by Gehrcke and Reichenheim<sup>1</sup> who observed rays streaming from heated salts of alkali metals when these were used as anodes in discharges. This discovery was made before good means of analysis were known, but from the visual spectrum of the rays they deduced rightly that these were positively charged ions of the metals concerned. They obtained the rays, which they called "anode rays" by two distinct methods. The first, which may conveniently be called the "hot anode" method, consisted in using as anode of the discharge tube a platinum strip coated with a salt of the metal and electrically heated by an external battery. The second method by which most of their pioneer work was done depended on the use of a mixed paste of graphite and salt, a "composite anode" which was automatically heated by the discharge itself.

**62. First analysis of the alkali metals.**—This was made by the writer<sup>2</sup> using the hot anode method by means of the apparatus indicated in Fig. 15. The heated anode A is a strip of platinum foil welded to stout leads fused through the glass at C, the mounting being arranged so that it could be easily removed and replaced. It was heated electrically as indicated and placed immediately opposite the perforation of the cathode and about 1 centimetre away from it. The platinum strip was bent at one end into a U-shaped channel into which

<sup>1</sup> Gehrcke and Reichenheim, *Ver. Phys. Gesell.*, 8, 559, 1906; 9, 76, 200, 376, 1907; 10, 217, 1908.

<sup>2</sup> Aston, *Phil. Mag.*, 42, 436, 1921.

salts could be fused. The discharge was maintained by a large induction coil and rectified by means of the valve V. The discharge tube was pumped out as completely as possible and then the anode cautiously heated until the discharge started. This usually happened at a dull red heat, and by very careful adjustment of the temperature and of the primary current in the coil it was possible, under favourable conditions, to maintain a fairly steady current of 1 to 2 milliamperes at a potential of about 20 kilovolts. There was very little visible glow in the tube, the X-radiation was small and, although a faint cloud of sodium light nearly always appeared in front of the red-hot anode, the pressure was too low for the anode rays to be visible; their point of impact with the cathode could, however, be inferred from the scintillations on its surface.

Observations of this effect lead to the conjecture that the bulk of the rays originate not from the surface of the salt itself but from that of the heated platinum, and also that some points on this are much more active than others, giving rise to jets of rays. The direc-

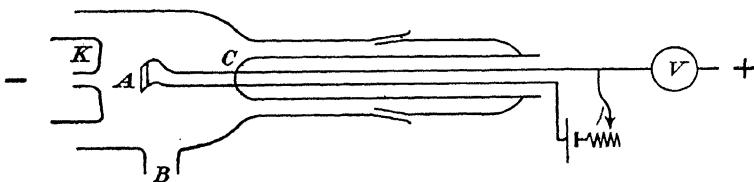


FIG. 15.—Hot Anode Discharge Tube.

tion of these jets seemed to depend on the local configuration of the strip and was beyond practical control. The obvious device of moving the anode about by means of the ground joint to get a radiant point in the required place could not be applied, for the parabolas were never bright enough to be visible on the willemite screen. To add to these difficulties the salt disappeared very rapidly, in some cases in a few minutes. Consequently exposures were very limited in duration, and even in the most favourable cases the results rarely had a satisfactory intensity.

On the other hand, as a means of identifying isotopes the method has the great merit of producing rays of the metals only. This characteristic seems to be due to the very low pressures used and also possibly to the position of the anode itself, which prevents any rays generated in the more distant parts of the tube from ever reaching the perforation in the cathode in the necessary axial direction.

The hot anode discharge was first tested by means of the parabola method of analysis and the most successful experiment was done with a mixture of sodium and lithium phosphates which contained

traces of potassium salts. By great good fortune a very strong jet of rays must have been directed along the axis and three satisfactory exposures were obtained before the anode dried up. One of these is reproduced in Plate I (5). A strong parabola at 7 and a weak one at 6 demonstrate clearly that lithium is a complex element, as its chemical atomic weight 6.94 leads one to expect. This result was announced jointly by the writer and G. P. Thomson,<sup>1</sup> who was then investigating rays from a composite anode. Soon after it was confirmed independently by Dempster.<sup>2</sup>

The apparatus was then attached to the first mass spectrograph and although the beams obtained were very feeble they were sufficient to identify the mass numbers of the isotopes of sodium, potassium, rubidium and caesium.<sup>3</sup>

**63. Method of accelerated anode rays.**—The technical difficulties involved in the hot anode method gave little promise of its successful application to the metals of other groups, so after an attempt had been made to apply the vacuum arc to the problem,<sup>4</sup> attention was again turned to the possibilities of the alternative device of the composite anode made of a paste of graphite mixed with metallic salts. This had already been successfully applied to the parabola method of analysis by G. P. Thomson.<sup>5</sup> After a number of possible improvements had been tried an arrangement was found by which the mass rays could be accelerated after production. This was capable of giving beams high enough in intensity and under sufficient control to be applied to the mass spectrograph.

The general form of the apparatus with which the best results were obtained is shown diagrammatically in the accompanying rough scale drawing (Fig. 16). The discharge tube is comparatively small and shaped as illustrated. The construction of the anode is indicated in detail on a larger scale. The graphite paste is pressed into a hole drilled in the end of a small steel cylinder. This is carried on a long brass wire so that it can be slid into a pyrex glass tube about 20 cm. long fitting it closely. The working position of the steel container is with its face containing the paste flush with the end of the tube which is cut off exactly at right angles. The thickness of the wall of the container is exaggerated in the sketch. It is actually made as small as possible consistent with strength, so that the anode looked at end on from the cathode appears simply as a graphite disc surrounded by a glass ring. Since the working of the apparatus is capricious and

<sup>1</sup> Aston and Thomson, *Nature*, **106**, 828, 1921.

<sup>2</sup> Dempster, *Phys. Rev.*, **18**, 417, 1921.

<sup>3</sup> Aston, *Nature*, **107**, 72, 1921.

<sup>4</sup> Aston, *Phil. Mag.*, **47**, 385, 1924.

<sup>5</sup> V. p. 126.

liable to be altered entirely in character by the slightest variation in the position of its parts, the anode container was so arranged that it could be withdrawn, refilled and replaced with great exactness. The best working position of the anode was as indicated. The discharge producing the anode rays took place between the graphite paste and the subsidiary cathode. The latter was an aluminium cylinder pierced for the passage of the rays and hollowed at its working surface to concentrate the cathode rays on the anode. It was mounted in a block of ebonite just in front of the earthed cathode of the mass-spectrograph.<sup>1</sup>

During the preliminary experiments when the cathode of the discharge tube itself was earthed, it was found in the first place that good beams of anode rays could only be obtained when the pressure

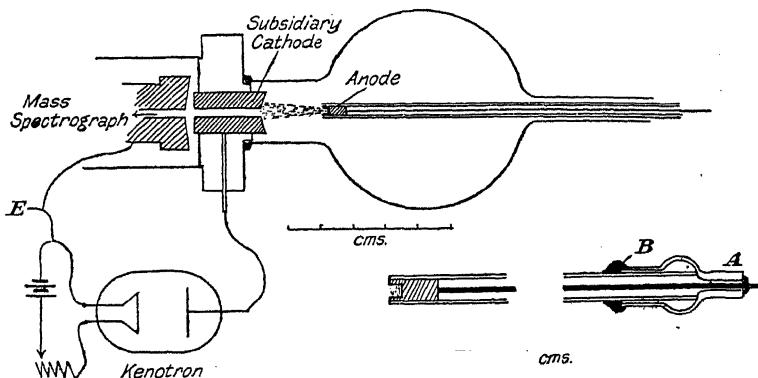


FIG. 16.—Apparatus for Accelerated Anode Rays.

in the discharge tube was comparatively high and the potential consequently too low to be convenient for use with the mass spectrograph. In the second place the discharge itself was exceedingly unstable, for increase of current meant a hotter anode; this led to the liberation of more gas which caused further increase of current. On the other hand, if the anode was allowed to get too cold, the tube went hard and ceased to conduct altogether.

Both these difficulties were overcome by the introduction of a secondary cathode connected to earth through a kenotron as indicated. For if the earthed filament of the kenotron is maintained at a definite temperature, sufficient, for example, to give a saturation current of 1 milliampere, it is impossible to force more than 1 milliampere through it. Hence, whatever the conditions of the discharge tube, short of absolute non-conductivity, the current through it will remain constant.

<sup>1</sup> V. Fig. 10.

It will be realized at once that this arrangement supplies exactly the stabilizing influence required. If the discharge tube gets harder, the potential drop between the anode and the subsidiary cathode will increase. The energy of the beam of cathode rays will increase, this will raise the temperature of the anode and soften the tube. On the other hand, if the tube gets too soft the energy of the cathode ray beam will decrease, cooling the anode and hardening up the tube again.

In addition, the main discharge can now be regulated to give rays of any required energy independent of the hardness or softness of the discharge tube. If we put a mean of 24 watts through the secondary circuit at a current of 1 milliampere, the anode will be maintained at a mean potential of 24 kilovolts above earth and the rays after leaving the subsidiary cathode will be *accelerated* to a velocity corresponding to that potential. Thus, if the potential between the anode and the subsidiary cathode is, say, 8 kilovolts, the accelerating potential will be 16 kilovolts; if the discharge potential falls to 6 kilovolts, the accelerating potential will automatically rise to 18 kilovolts and so on.

For details of the experimental procedure the reader is referred to the original paper.<sup>1</sup>

It has not yet been found possible to obtain a beam of anode rays sufficiently strong for any mass line to be visible on the willemite screen as are the lines of hydrogen with the discharge-tube method. On this account the first three or four minutes of the discharge are generally utilized in recording the lithium lines as a necessary check on the working of the whole apparatus.

With all elements other than the alkali metals the effects are feeble, so the exposures are prolonged as far as possible until the anode dries up or it is judged that further continuation is useless. Most of the results, when the apparatus was working particularly well, were obtained with exposures of about half an hour, but in some cases the discharge was maintained for one hour and a half.

At the beginning of the discharge the anode surface is comparatively cool and glows brilliantly red showing the lithium spectrum. The bright divergent beam of lithium anode rays never lasts many minutes of the exposure. Its appearance is a good sign, but equally bright lithium mass lines have been obtained when it could not be seen at all. A valuable indication that the anode surface is functioning properly is the appearance of a small cloud of sodium light surrounding it exactly as in the case of the hot anode experiments.<sup>2</sup>

As the gases come off less and less rapidly from the anode intermittent pumping only is required to keep the pressure down and the longer portion of the exposures is generally carried out without pump-

<sup>1</sup> Aston, *Phil. Mag.*, **47**, 385, 1923.

<sup>2</sup> V. p. 65.

ing at all. The anode by now has lost its lithium glow and becomes red and sometimes white hot. Lithium mass rays are probably absent at these later stages, but the lines of the heavier members of the alkali group, if they are present in the anode paste, still continue to come off with undiminished intensity and in the case of other elements the high temperature of the anode surface seems favourable and may be essential. The general glow of the discharge is dirty yellow at the start and becomes blue-grey in the later stages.

**64. Experimental results.**—The principal difficulty in the way of successful working of the method is complete ignorance of the mechanism of the discharge which is probably very complex. It behaves at times in the most capricious and unaccountable manner. Each time the discharge tube is altered or even taken down for cleaning entirely different results may be obtained. When by good fortune all is well the arrangement is capable of good performances. Thus, after a favourable setting of the apparatus six elements were successfully analysed in as many working days. On the other hand, after dismantling became imperative and it had been cleaned and rebuilt, exactly as before as far as one could tell, no results of any value were obtained during weeks of work.

The method appears to be capable of wide application to metallic elements. Those of Group I are much the easiest to deal with, and those of Group IV apparently the hardest. The difficulty of obtaining the mass rays appears to increase with increasing atomic weight, an effect which may be partly ascribed to decreasing velocity of the rays. The quantity of material necessary is only a few milligrams, of which much can be recovered after the experiment, so that it is particularly suitable in cases where only small quantities are available. High purity, as in other mass spectrum measurements, is in general of quite subordinate importance.

In the matter of interpretation the results of accelerated anode rays are very nearly ideal. The ordinary discharge method gives altogether too many lines due to atoms and molecules other than those under consideration; the hot anode method gives too few, rendering measurement difficult. The method gives practically no molecular lines at all and the atomic ones generally present are just about what is required for a satisfactory system of reference, and no more. The most important of these lines are  $^{12}\text{C}$ ,  $^{27}\text{Al}$ ,  $^{28}\text{Si}$ ,  $^{56}\text{Fe}$ ,  $^{127}\text{I}$ .

Thanks to the very wide range of application of this method the mass spectra of over twenty elements, including several of the rare earths, were successfully obtained by its use with the first mass spectrograph. The extension of these results to apparatus of higher resolving power will be described later.

**65. Dempster's analysis of anode rays.**—Dempster's original apparatus for the analysis of anode rays derived from heated salts has already been described (p. 28). His later<sup>1</sup> modification of the apparatus in which the metals themselves were vaporized is shown in Fig. 17. The anode is a small iron cylinder filled with metal and heated electrically by a surrounding coil of iron alloy wire. The vapour so produced is ionized by bombardment with electrons which have fallen through 30–160 volts from a coated platinum strip near the mouth of the cylinder F. The positively charged ions pass into the accelerating field through a hole in the iron plate P. The energy of the rays before acceleration is regarded as being negligibly small, so that all of them reach the slit S<sub>1</sub> with the same energy which can be controlled by varying the potential between P and S<sub>1</sub>. This potential is usually 800 to 1000 volts derived from a set of small storage cells. The rays passing downwards in a narrow beam through S<sub>1</sub> are bent into a semicircle by the magnetic field and so focused upon the second slit S<sub>2</sub>. Here they are detected and measured by the charge they bring up to a plate as before.

#### *Methods of measurement.*

—The quadrant electrometer used in the first experiments to detect the rays is replaced by a Wilson tilting electro-

scope and the compensating arrangement illustrated. The positive current carried by the rays to the plate is balanced by an equal negative ionization current driven to the electrode of the ionization chamber L. The electrostatic balance is indicated by the quadrant electrometer. The novel feature of the arrangement is the method used for adjusting the ionization current to balance the positive ray current. The ionizing agent is a group of old radium emanation tubes which are placed as indicated and cut off from the ionization chamber by an adjustable graduated slit. A slit width of 1 millimetre gives an

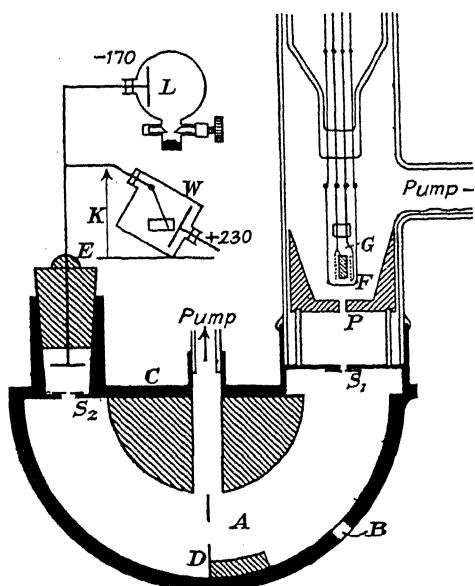


FIG. 17.—Dempster's Modified Apparatus (1922).

<sup>1</sup> Dempster, *Phys. Rev.*, **20**, 631, 1922.

ionization current of approximately  $6 \times 10^{-12}$  amperes. Settings for balance can be made in about 5 seconds to within  $\frac{1}{40}$  mm.

In order to bring rays of different mass to the slit  $S_2$ , either the electrical potential or the magnetic field may be altered.<sup>1</sup> In practice the latter cannot be conveniently measured, so it is kept constant and the accelerating potential put through a series of measured values. If the current reaching the plate is plotted against potential, a curve is obtained showing peaks corresponding to the different isotopes.

This change in the accelerating potential between  $P$  and  $S$ , is responsible for a serious source of error in the measurements of the relative

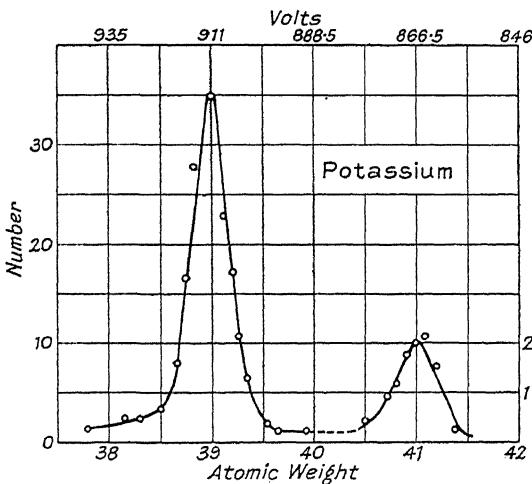


FIG. 18.—Curve for Potassium.

intensity of isotopes which was not detected by Dempster in his earlier experiments. It was due to the stray electric field spreading through the hole in  $P$  and affecting the flow of the ions through it, and was later rectified by the use of gauzes.<sup>2</sup>

**66. Experimental results.**—A typical curve obtained in this way with potassium is shown in Fig. 18. In this experiment the peak corresponding to the stronger isotope 39 occurred at 911 volts. The whole-number rule is assumed and the maximum is placed exactly at 39, and the other atomic weight abscissæ are obtained by dividing  $39 \times 911$  by the potential in volts for each measurement. The current scale for the fainter isotope in the figure is made five times that for the stronger. The intensity ratio is approximately 18 to 1, giving a mean atomic weight of 39.1 in good agreement with the chemical value.

<sup>1</sup> V. equation on p. 28.

<sup>2</sup> Dempster, *Phys. Rev.*, **20**, 636, 1922.

The position of the peaks confirms the result obtained with the hot anode.<sup>1</sup> Dempster independently demonstrated the isotopes of lithium but was unable to obtain consistent values for their relative proportions in the element for the reasons already mentioned. The most important analysis obtained by this method are those of magnesium, calcium and zinc.

**67. Other sources of anode rays.**—Other sources of positive ions suitable for analysis were developed later. Kunsman<sup>2</sup> discovered that the crystal granules used as catalysts in the synthesis of ammonia when heated emitted positive ions at a remarkably constant rate. These granules consist of a fused mixture of iron oxide with about 1 per cent. of an alkali or alkaline earth metal with sometimes the addition of about 1 per cent. of aluminium oxide. A rough analysis of the rays produced by means of a low-resolution magnetic spectrograph of the Dempster type showed that the ions were singly charged atoms of the metals concerned.<sup>3</sup> Kunsman sources have been extensively used for experiments on positive ions, for unlike the other anode sources so far described they will work at exceedingly low pressures. On the other hand, their life seems to be limited to  $\frac{1}{2}$  to 2 hours and the intensity of the beams produced has, so far, not been found high enough for analyses of high resolution. It has been noticed that the strongest jets of rays from a Kunsman source, like those from the "hot anode" usually originate from the metal heater at the edge of the fused mixture rather than from the mixture itself.

This fact led Moon and Oliphant<sup>4</sup> to prefer as a source a heated tungsten filament immersed in the vapour of the metal. The theory of this has been discussed by Langmuir and Kingdon<sup>5</sup> who predict perfect efficiency—that is, all the atoms striking the filament will be ionized—when the work function greatly exceeds the ionization potential. Both in steadiness and intensity this form of source is admirable, but unfortunately its scope is limited so far to a few easily ionizable metals which can be conveniently vaporized.

For their work on potassium and rubidium Bondy, Johannsen and Popper<sup>6</sup> heated pyrex glass containing alkaline salts. In the more recent work on separation of the isotopes of the alkalis,<sup>7</sup> Kunsman sources of great intensity and endurance have been used.

<sup>1</sup> V. p. 144.

<sup>2</sup> Kunsman, *Science*, **62**, 269, 1925; *Proc. Nat. Acad. Sci.*, **12**, 659, 1926.

<sup>3</sup> Barton, Harnwell and Kunsman, *Phys. Rev.*, **27**, 739, 1926.

<sup>4</sup> Moon and Oliphant, *Proc. Roy. Soc., A*, **137**, 463, 1932.

<sup>5</sup> Langmuir and Kingdon, *ibid.*, **A**, **107**, 61, 1925.

<sup>6</sup> Bondy, Johannsen and Popper, *Zeit. Phys.*, **95**, 46, 1935.

<sup>7</sup> V. p. 257.

## CHAPTER VIII

### EARLY INSTRUMENTS OF PRECISION

As theory discussed later will show, the Whole Number Rule established by the first mass spectrograph was never supposed to be mathematically exact. Although the deviation was only measurable with any accuracy in the single case of hydrogen it was soon clear that the masses of the lithium isotopes 6 and 7 exceeded whole numbers by at least 1 part in 1000, the mass of carbon being taken as exactly 12, while those of other atoms such as  $^{56}\text{Fe}$  appeared to be less than whole numbers.<sup>1</sup>

**68. Costa's mass spectrograph.**—The first attempt to measure these deviations by measurements of an accuracy greater than 1 in 1000 was made by Costa who in 1925 published results obtained by means of a mass spectrograph set up in Paris.<sup>2</sup> This instrument was identical in principle with the first mass spectrograph, but included certain refinements which enabled its designer to claim for it comparisons of mass to an accuracy of 1 in 3000, that is to say, three times greater than that previously attained. With this apparatus Costa compared, by the method of bracketing<sup>3</sup> Helium with Hydrogen, Helium with Carbon, Helium with Lithium 6 and Nitrogen with Lithium 7. His work on lithium is of the greatest importance. In it he overcame the very serious experiment difficulties of recording the mass rays of lithium and those of nitrogen in the same discharge tube by means of a movable anode. The values of the two lithium isotopes recalculated from his ratios were the only ones available for some years.

**69. Aston's second mass spectrograph.**—Improvements in the design of the first mass spectrograph had been under consideration as early as 1921. It was realized that the accurate determination of the divergences from the whole-number rule, now called packing fractions, was of fundamental importance since this is one of the few avenues by which the problem of the structure of the nuclei of atoms could be approached. Every effort was made to push the precision

<sup>1</sup> Aston, *Phil. Mag.*, **45**, 941, 1923.

<sup>2</sup> Costa, *Ann. Physique*, **4**, 425, 1925.

<sup>3</sup> V. p. 51.

## ASTON'S SECOND MASS SPECTROGRAPH

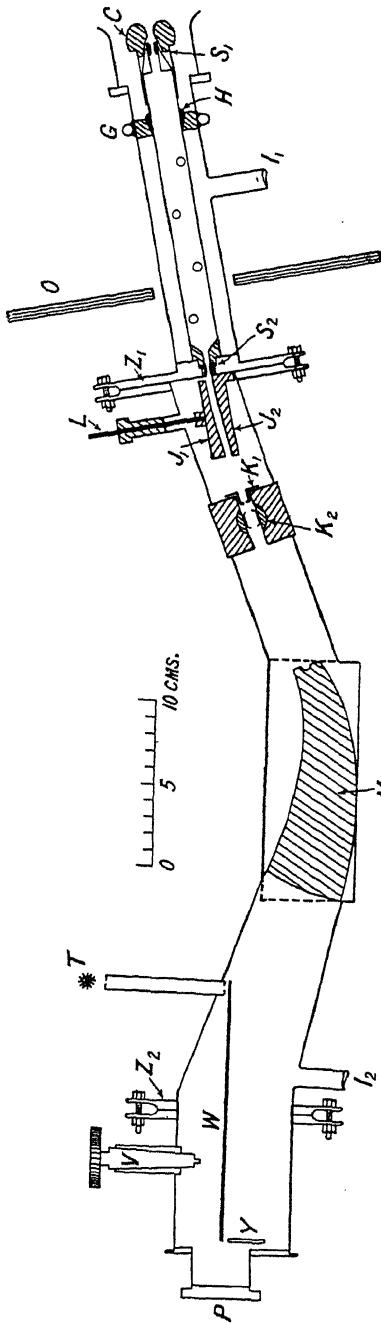
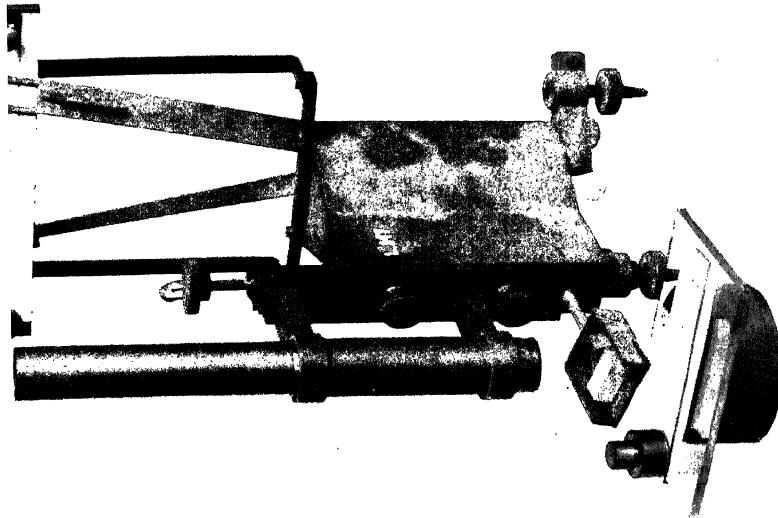


FIG. 19.—Diagram of Aston's Second Mass Spectrograph.

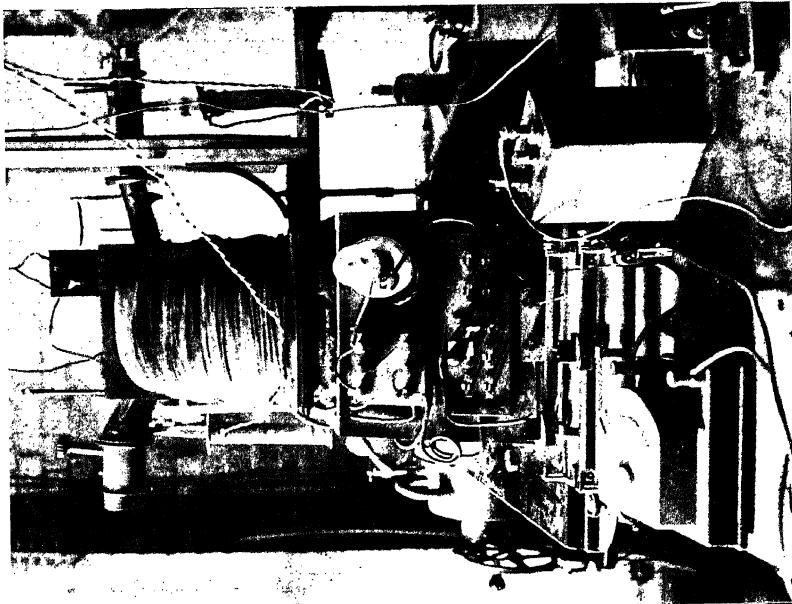
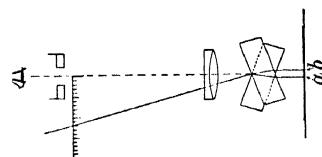
of analysis to its practical limit. It was finally decided that the increase of resolving power could best be obtained by doubling the angles of electric and magnetic deflection and using finer slits placed further apart. Special methods were devised for increasing the accuracy of comparison. These objects were successfully carried out. The improved instrument was set up by the writer in the Cavendish Laboratory in 1925<sup>1</sup> and used with slight modifications during the following ten years. It had five times the resolving power of the first one, far more than enough to separate the lines of any element known, and its accuracy of measurement approached 1 in 10,000, which is just sufficient to give rough first order values to the divergences from whole numbers. The general appearance of the instrument can be gathered from the photograph (Plate V) and the details of its construction from the diagram (Fig. 19) which is drawn approximately to scale.

**70. Slit system and deflecting fields.**—To improve the collimation of the rays the slits were 20 cm. apart, double the distance used before, and so arranged as to be easily replaceable. The electric deflection was increased to one-sixth of a radian, and produced by

<sup>1</sup> Aston, *Proc. Roy. Soc., A*, **115**, 487, 1927.



THE COMPARATOR.



ASTON'S SECOND MASS SPECTROGRAPH (1925-1935).

slightly different, and, finally, the two in series  $2V + h$  could be applied rapidly over and over again. The length of the exposures at the first two potentials, giving lines of the molecule, relative to the third, giving the line of the atom, could be controlled and were adjusted to give lines of equal intensity. A ratio of precisely 2 to 1 should give three lines forming an exactly symmetrical bracket. This device eliminates the necessity of keeping the magnetic field absolutely constant since the electric fields are changed so rapidly that small changes will only lessen the sharpness of the lines and not alter their relative positions. It also makes it unnecessary to measure any potential at all so long as  $h$  is less than 1 per cent. of  $V$ . It is, in fact, the exact counterpart of finding the mid-point of a line with a pair of dividers, and like this can, unfortunately, be applied only to ratios of 2 to 1. Measured by this means and allowing for the electron correction, the polarization effect, even with clean gold surfaces, was found to be still as high as  $5 \times 10^{-4}$ , much too high to be neglected. Experiments made while it was very much greater had, however, shown that it remained very constant so long as the conditions of discharge were not altered, so it was decided to eliminate it as far as possible by using the rays themselves to measure the ratios of the field strengths.

**72. Performance of the instrument.**—The general appearance of the mass spectra obtained by means of the instrument in its present adjustment is shown by the reproductions on Plate VI. The spectrum photographed is nearly 16 cm. long and includes slightly more than one octave of mass. As Spectrum VI clearly shows, the distribution is surprisingly linear all along. The dispersion scale varies from about 1.5 mm. at the most deflected end, to rather more than 3 mm. at the least deflected end, for a change of mass of 1 per cent. Hence, in the middle portion of the plate the scale is about as open as that of a twenty-inch slide rule. The resolving power is sufficient to separate lines differing by 1 in 600 and as expected from the theory is not very different at the two ends. Since the lines are irregularly curved and change their shape as one moves from one end of the spectrum to the other, it is impossible to assign positions to them relative to the fiducial spot with sufficient accuracy to approach the figure of 1 in  $10^4$  aimed at. This can only be done by measuring the distance between lines of approximately the same intensity, and therefore the same shape, when they are quite close together.

**73. The comparator.**—Of several methods tried, the most convenient for making such a measurement is by an application of the principle of Poynting's Tilting Plate Micrometer.<sup>1</sup> If an object is observed through a thick plate of glass and the plate tilted, the object

<sup>1</sup> Poynting, *Phil. Trans., A*, 204, 413, 1905.

will appear to shift. Poynting showed that for moderately small angles, this shift is very exactly proportional to the tangent of the angle of tilt. For the present purpose, two plates are used with their edges touching. Their plane of separation is arranged to lie along the middle of the spectrum, which is observed directly below. The plates are so connected by a simple mechanism that they move through equal and opposite angles, giving double the range of a single plate and affording complete optical compensation for focus, so that fairly high powers of magnification can be used when calibrating with a standard scale. To measure the distance between two neighbouring lines *a* and *b* (Plate V), these are observed through a suitable low-power lens and the plates tilted until the edge of the right half of *a* coincides with the edge of the left half of *b*, giving the appearance of a single line if the intensities are equal. The tangent reading is taken and the operation reversed until the edge of the left half of *a* coincides with the edge of the right half of *b*. The sum of these two readings from the central zero is a measure of the distance and can be calibrated once and for all by the use of a standard scale. The great advantage of this over other types of comparator, for this particular purpose, is that the setting is practically independent of small changes in the position of the eye of the observer. By a lateral movement of the eye one can shift the dividing plane right across the narrow spectrum, and so compare any part of one line with the corresponding part of the other. This enables much more reliable readings to be obtained with irregularly shaped but similar lines than would a fixed line of division. A photograph of the instrument itself is shown in Plate V. It is at present fitted with two echelon plates 1 cm. thick. The measuring arm is 30 cm. long, and the tangent scale divided into millimetres 78·5 of these correspond to 1 mm. shift. With sharp lines the accuracy of setting is well within 0·01 mm., but the range is small, a little more than 2 mm. The fainter the lines on these spectra the sharper they are, so that the best measurements are to be obtained from lines just strong enough to be clearly seen. In order to increase contrast, the plates are laid face down on glazed process paper and observed by reflected light. In some cases the negatives were intensified before measurement. The position on the spectrum of the pair of lines to be measured is at our disposal, and is chosen to suit the particular system of measurement employed. All the most accurate determinations were made in that part of the spectrum where the dispersion constant is about 3 mm. for 1 per cent. change of mass.

**74. Methods of measuring ratios of mass.**—The accurate comparison of two masses giving lines on a mass spectrum depends on the determination of two quantities, the distance between the lines,

and the dispersion constant. The first must be small, and is measured directly by the comparator as described. The second is arrived at indirectly by approximate measurements of large intervals between lines whose mass differences are known with sufficient certainty. The hydrides of carbon and oxygen are most useful for this. From these data, the dispersion constant for several points on the small range actually used can be plotted. These lie on a straight line, so that interpolation is easy. Values of the dispersion constant appear reliable to about 0·3 per cent. They are only constant for one setting of the apparatus, and must be confirmed or recalculated if any change is made. It will be seen that if the interval between the lines corresponds to a difference of mass of less than 1 per cent., and no other errors are present, an accuracy of 1 in 30,000 can be looked for. These measurements can be applied in a number of different ways to suit particular cases, the principal ones so far used can be classified as follows :

*Method I.*—Direct measurement on a single spectrum. This Method is virtually free from all uncertainty and independent of the polarization error, but can only be applied to bodies giving lines clearly resolved, but differing by less than 1 per cent. in mass. These cases are unfortunately very rare. The best example is the doublet given by oxygen, methane shown in Spectra I and IV. Here the lines only differ by 0·2 per cent. in mass, and can be obtained of equal intensity by manipulation of the quantities of oxygen and methane present in the discharge tube. Other cases will be noted later as they occur.

*Method II*, which may be called the method of series shift, can be employed whenever the masses to be compared form terms in a series whose unit of difference is not too great. Two potentials are chosen which will bring consecutive terms into the desired contiguity, and these are applied to the electric plates alternately during the exposure while the magnetic field is kept constant. The relative duration of the application of the potentials is adjusted to give, in the double spectrum produced, equal intensity to those two lines between which the interval is to be measured. A good example of this is afforded by the lines of bromine and its hydrides. These give a series 79, 80, 81, 82, shown in Spectrum V. First potentials 300 and 324 volts were applied alternately, giving four times longer exposure to the latter to compensate for the weakness of the HBr lines. In this way, Spectrum IIa was produced on which the small intervals 79, 80 and 81, 82 could be measured. The same operation was then repeated with the relative exposures reversed, giving Spectrum IIb and the interval 80, 81. Now, it is obvious that whatever the value of the dispersion constant, so long as its variation along the plate is smooth, if the four lines form a true progression, the interval 80, 81 must be the mean of the intervals

79, 80 and 81, 82, each of which correspond to the addition of one hydrogen atom. When, as in this case, it is not, the divergence from the mean so measured gives at once the relation between the masses  $^{79}\text{Br}$  and  $^{81}\text{Br}$  required.

*Method III.*—This is the method most generally applicable for which the instrument was designed. It is the original bracketing method modified by the use of small intervals instead of brackets. If we wish to find the ratio of an unknown mass  $x$  to a known mass  $a$  we must photograph their respective lines in virtual coincidence, that is to say near enough for exact determination of the interval as described above. This is done by applying suitable potentials  $V_1$ ,  $V_2$  whose ratio differs by about a half per cent. from the expected ratio  $x : a$ . As we cannot trust the deflecting fields to be exactly measurable by the potentials applied, on account of the polarizing effect, two other masses must now be found,  $b$  and  $c$ , whose ratio is identical or nearly so with  $x : a$ . The small interval  $x, a$  is photographed at the most advantageous position on the plate by applying the potentials  $V_1$ ,  $V_2$  in rapid succession alternately, keeping the magnetic field  $H_1$  constant. Then, using the same pair of potentials and a different magnetic field  $H_2$ , the small interval  $b, c$  is photographed on another spectrum. The magnetic field in this case is so chosen as to bring both intervals into the same region of the plate to diminish as far as possible errors due to the values of the dispersion constant. The intervals of length are now measured and transformed into intervals of mass by multiplying by the dispersion constants calculated for the mid-point of each interval. From the value of the interval  $b, c$ , so determined, and the known ratio of the masses concerned the effective ratio of the fields can be exactly calculated and then applied, by means of the interval  $x, a$ , to determine the mass  $x$ . In practice it is not usually necessary to evaluate the ratio of the fields, for the masses concerned are all so near whole numbers that the divergence of  $x$  from a whole number is simply the difference between the mass intervals, corrected by additions or subtractions of the known divergences of the other masses used. If the agreement between the ratios  $x : a$  and  $b : c$  is only numerically approximate, and the approximation of suitable order, the voltage ratio is adjusted to lie between them and the sum of the mass intervals used. The accuracy in this case will not be so high. An example of this method of comparison will be seen in Spectra III and IV. The first is a double spectrum taken with methane using a potential ratio between 15 : 12 and 24 : 19. The second is taken on the same plate with the same potentials after the magnetic field had been increased and  $\text{BF}_3$  introduced. The sum of the intervals seen at the right hand of the spectra gives the relation between carbon and fluorine.

**75. The first packing fraction curve.**—The first important piece of work performed with this instrument, and the one for which it was primarily designed, was the measurement of the divergences of the masses of atoms from whole numbers. For a variety of reasons<sup>1</sup> the atom  $^{16}\text{O}$  was chosen by the writer as the most suitable standard, and the percentage deviations of the masses of other atoms from whole numbers on the scale  $^{16}\text{O} = 16$  were expressed in parts per 10,000 and called "packing fractions," since they are a measure of the closeness of packing of the electrical particles forming the nuclei of the atoms concerned. Put in another way, if we suppose the natural numbers and the masses of the atoms to be plotted on a uniform logarithmic scale, such that every decimetre equals a change of one per cent., then the packing fractions are the distances expressed in millimetres, between the masses and the whole numbers.

In 1927 by the application of the various methods just

<sup>1</sup> V. p. 197.

#### DESCRIPTION OF THE MASS SPECTRA REPRODUCED IN PLATE VI

I.—Single spectrum of the  $\text{C}_1$  group, showing oxygen methane doublet.

II.—Double spectra illustrating comparison of Br lines by Method II.

III.—Double spectrum comparing  $\text{CH}_3$  and  $\text{C}_2$  voltages 280, 352. The oxygen methane doublet is seen on the extreme right.

IV.—Double spectrum comparing F and  $\text{C}_2$ , voltages 280, 352. This combined with III gives the mass of fluorine in terms of carbon and hydrogen by the general Method III. The line of  $^{11}\text{B}$  can be seen and, very faintly, that of  $^{10}\text{B}$ . The oxygen methane doublet is shown very clearly in the lower potential spectrum.

V.—Single spectrum taken with  $\text{CH}_3\text{Br}$  showing the pairs of lines due to Br, HBr,  $\text{CH}_2\text{Br}$  and the second-order mercury group.

VI.—Double spectrum comparing  $^{81}\text{Br}$  with  $\text{CO}_2$ , voltages 300, 324. The higher voltage spectrum, which had an exposure of half an hour, shows the triply-charged Br line at 26.3. It contains the lines of sulphur, chlorine, etc., and is an admirable illustration of the linear distribution of lines differing by one unit.

VII.—Double spectrum showing the lines of phosphorus and its hydrides photographed between the lines of carbon monoxide and phosphorus.

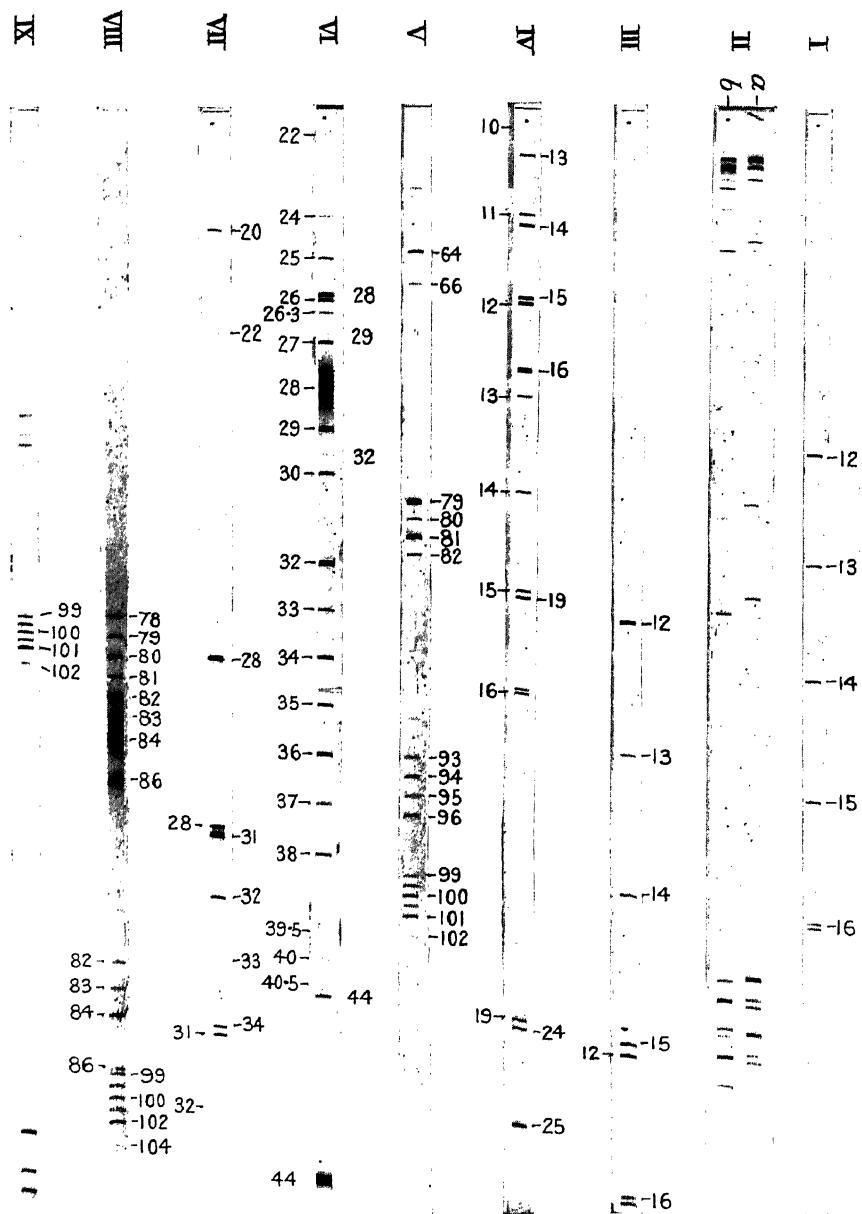
VIII.—Double spectrum comparing  $^{86}\text{Kr}$  with  $^{198}\text{Hg}$ . The lines of krypton are seen near the middle. The second-order lines of mercury are shown under high dispersion.

IX.—Spectrum showing the second-order mercury group very clearly.

X.—(a) and (b) Spectra showing the even spacing of the tin monomethyl and xenon lines. (c) The same with long exposure showing the isotopes of tin.

XI.—Six double spectra taken with the same voltages 360, 368. Each has an exposure suited to a particular pair of lines, for comparison of  $\text{CO}_2$ , Kr and Br. (a)  $^{86}\text{Kr}$  :  $\text{CO}_2$ , (b)  $^{78}\text{Kr}$  :  $^{80}\text{Kr}$  and  $^{80}\text{Kr}$  :  $^{82}\text{Kr}$ , (c)  $^{80}\text{Kr}$  :  $^{82}\text{Kr}$  and  $^{82}\text{Kr}$  :  $^{84}\text{Kr}$ , (d)  $^{82}\text{Kr}$  :  $^{84}\text{Kr}$ , (e)  $^{84}\text{Kr}$  :  $^{86}\text{Kr}$ , (f) after addition of methyl bromide,  $^{79}\text{Br}$  :  $^{81}\text{Br}$ .

PLATE VI

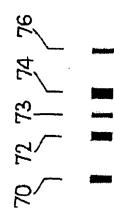


TRA TAKEN WITH THE SECOND MASS SPECTROGRAPH, 1925, 1926, 1927.

PLATE VII



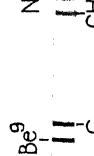
Zinc.



Germanium.



Tellurium.



$\text{CH}_2$

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described about a score of elements had yielded results, and it was possible by plotting packing fraction against mass number to obtain the exceedingly interesting packing fraction curve shown in Fig. 20. It will be seen that starting with a very high positive value for hydrogen the curve drops steeply through lithium and boron, and crossing the zero line in the region of neon descends to a minimum in the region of iron and nickel. It then rises gradually and recrosses the zero line near mercury. Helium, carbon and oxygen lie below the curve, a fact seen to be in good agreement with the observations of Lord Rutherford of the extreme stability of the nuclei of these elements under bombardment with alpha particles. The same authority pointed out that the very gradual slope of the curve in the region of high atomic

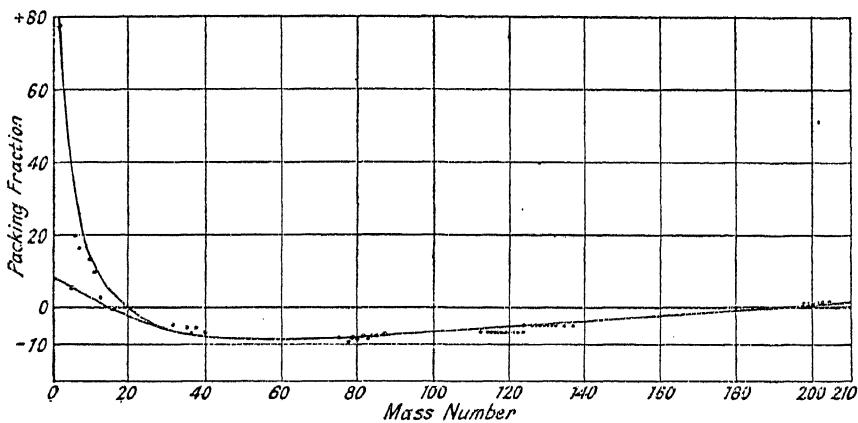


FIG. 20.—Aston's Original Packing Fraction Curve (1927).

weights supplied a good explanation of the fact that the positive particles expelled by naturally radioactive elements are alpha particles and not protons.

The most valuable implications of the packing fraction curve are clearly in the subject of sub-atomic energy, where it is second only in importance to the basal fact, demonstrated some years before by the first mass spectrograph, that four hydrogen atom do actually weigh more than one helium atom. It depicts in a general way the changes of energy to be expected from transmutations of nuclei, not only by the aggregation of light atoms to form heavier ones, but also the prodigious release of energy to be expected from the fission of uranium by neutron bombardment, a phenomenon entirely undreamt of when the curve was first drawn.

**76. Analysis of the rare earths and other elements.**—After the demonstration of the packing fraction curve the instrument was used

to develop the method of measuring isotopic abundance by photometry which will be described in the next chapter, and at the same time to continue the search for new isotopes. The most serious gap in knowledge at that time was the group known as the rare earths, and aided by improved vacuum technique a systematic attack was made on these in 1934<sup>1</sup> by the method of accelerated anode rays. The apparatus for producing the rays from the halide compounds of the elements was virtually identical with that shown in Fig. 16, the only noteworthy improvement being the provision of a continuous stream of iodine vapour through the discharge tube. As the object was the detection of weak components rather than measurement of mass, wide slits were employed and some thirty odd new isotopes discovered. Later hafnium was analysed and further search continued until in 1935<sup>2</sup> only four elements remained without mass spectrum data.

**77. Bainbridge's mass spectrograph.**—The apparatus with which Bainbridge obtained such valuable results during the period

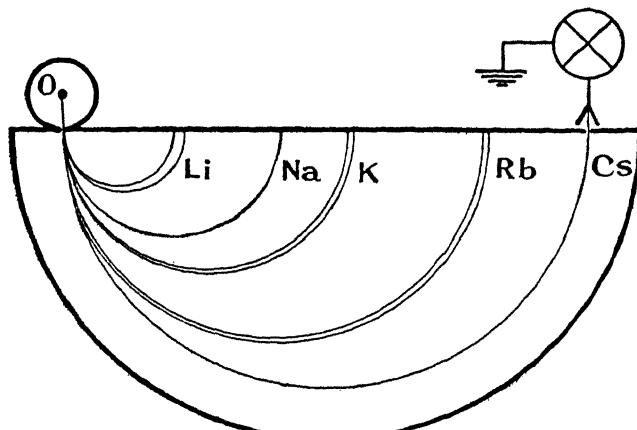


FIG. 21.—Diagram of Analysis of Alkali Metals.

1930–5 was built in the laboratory of the Bartol Research Foundation of the Franklin Institute. A preliminary description of it appeared in 1930.<sup>3</sup> It was originally intended to work on the principle used by Dempster,<sup>4</sup> and to extend his work to the heavier elements. As this requires semicircular focusing together with much increased resolution its main feature is a very large electromagnet. This is so designed as

<sup>1</sup> Aston, *Proc. Roy. Soc., A*, **146**, 46, 1934.

<sup>2</sup> Aston, *ibid.*, **A**, **149**, 396, 1935.

<sup>3</sup> Swann, *J. Franklin Inst.*, **210**, 751, 1930.

<sup>4</sup> V. p. 28.

to give a uniform field, up to 15,000 gaus, over a semicircular area of 40 cm. diameter with a 1.8 cm. gap.

The apparatus was first used to investigate the isotopes of the alkali metals<sup>1</sup> and the blackening effect of their ions on photographic plates.<sup>2</sup> For this work it was arranged as indicated in the diagram (Fig. 21). Heated natural silicates of the elements provided the ions and were coated on a platinum strip forming the hot anode source at O. These ions were then accelerated by potentials up to 2000 volts to give a homogeneous beam of mass rays which were analysed by the magnetic field as indicated in the diagram exactly as in Dempster's apparatus. The current carried by the rays was collected and measured by an electrometer as shown. On account of the high resolving power available it was possible to make a critical search for unknown isotopes, and measure the relative abundance of the isotopes of lithium more accurately than hitherto possible.

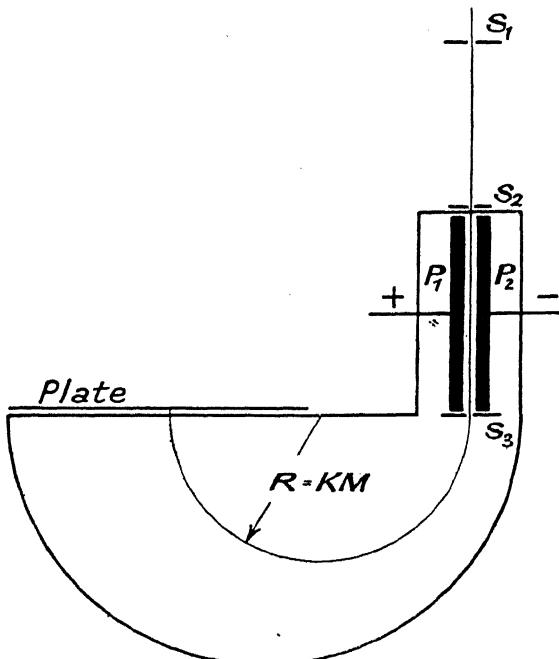


FIG. 22.—Diagram of Velocity Selector.

**78. Method of the "velocity selector."**—The number of elements to which the arrangement described above can be applied is very limited and to extend the use of the instrument to mass rays

<sup>1</sup> Swann, *J. Franklin Inst.*, 212, 317, 1931.

<sup>2</sup> V. p. 88.

produced by ordinary discharges Bainbridge applied to it a new and original principle illustrated in Fig. 22. In this the stream of rays to be subjected to semicircular focusing is not homogeneous in energy, as in Dempster's method, but homogeneous in velocity. The beam of ions produced by an ordinary discharge is collimated by the slits  $S_1$ ,  $S_2$  and then passed through a "velocity selector" in which their

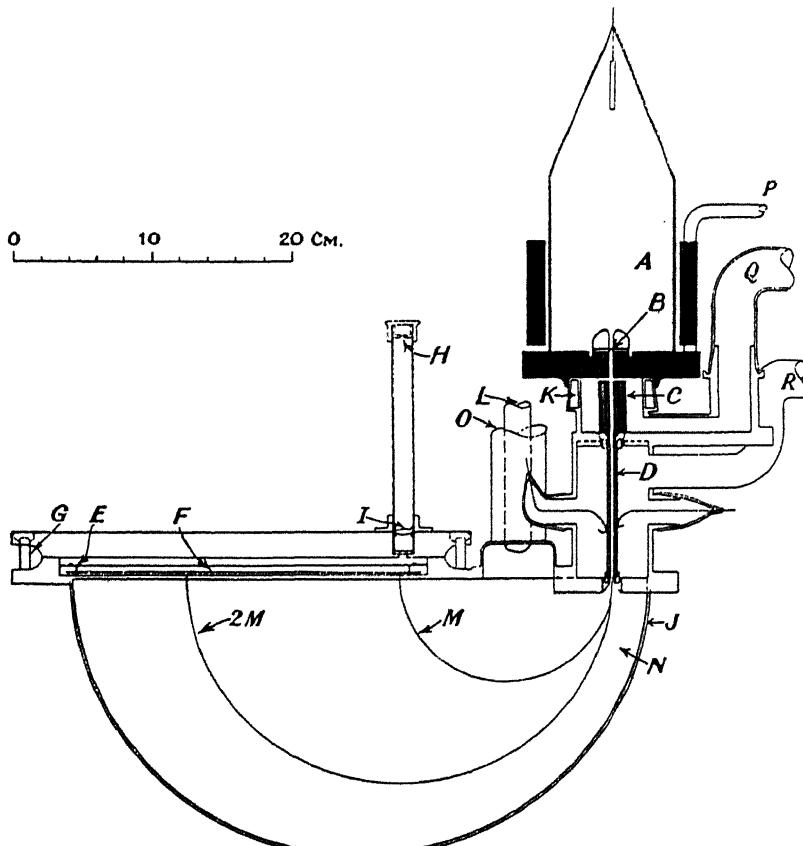


FIG. 23.—Diagram of Bainbridge's Mass Spectrograph.

deflexions are balanced by opposed electric and magnetic forces. Ions which traverse this section of the apparatus without deflexion all have the same velocity  $v$ , proportional to  $X/H$ , within narrow limits, where  $X$  is the electric force between the plates  $P_1$ ,  $P_2$ , and  $H$  is the magnetic field intensity perpendicular to the electric field. The ions which emerge from slit  $S_2$  at the far end of the velocity selector are introduced into a uniform magnetic field, the camera section of the apparatus,

and fall upon the surface of a photographic plate after describing a circular path for  $180^\circ$ . The radius of curvature of a mass  $m$  with charge  $e$  is proportional to  $mv/eH$  where  $H$  is the magnetic field in this region, that is to say proportional to the mass of the ion, so that the mass scale is linear. Fig. 23 is a drawing to scale showing details of the apparatus. The rays are generated in a Wien type discharge tube at potentials of 5000 to 20,000 volts and enter the velocity selector D through a fine slit. The region intermediate between the discharge tube and the velocity selector is evacuated through Q by a fast condensation pump. The rays strike the photographic plate F normally, and the mass scale is practically perfectly linear, having a dispersion of 1.6 mm. at one end and 3.8 mm. at the other for a mean difference of 1 per cent.

**79. Experimental results.**—Some of the mass spectra obtained by Bainbridge are illustrated in Plate VII. Those of zinc and germanium were of particular value as they eliminated certain lines, previously announced as isotopes, which were in fact due to hydrides.<sup>1</sup> The spectra obtained with tellurium revealed three new rare isotopes of that element. Bainbridge was the first to photograph the doublet formed by the doubly charged line of helium and the hydrogen molecule, and by it obtain a direct measurement of the hydrogen helium ratio of mass.<sup>2</sup> He was also the first to measure the isotopic weight of the newly discovered heavy hydrogen<sup>3</sup> by means of the doublet shown in the Plate. Of even greater general interest was his success with this apparatus in obtaining the mass lines of light metallic elements such as beryllium, shown in the Plate, at the same time as standard comparison lines, a matter of extreme technical difficulty. By establishing accurate comparisons of the masses of the light particles concerned in nuclear disintegrations, particularly that of  $^7\text{Li}$ , discovered by Cockcroft and Walton, he achieved a noteworthy triumph in the experimental proof of the fundamental theory of Einstein of the equivalence of mass and energy.<sup>4</sup>

<sup>1</sup> V. p. 61.

<sup>2</sup> V. p. 119.

<sup>3</sup> V. p. 120.

<sup>4</sup> Bainbridge, *Phys. Rev.*, **44**, 123, 1933.

## CHAPTER IX

### MEASUREMENTS OF ABUNDANCE

**80. Methods of determining the relative abundance of isotopes.**—The determination of the relative abundance of the isotopes of a complex element is of fundamental importance<sup>1</sup> and in addition affords a means of determining its chemical atomic weight by purely physical means. The most direct and general method is by some form of mass ray analysis. The first quantitative measurements of the kind were made by Sir J. J. Thomson<sup>2</sup> who brought the parabolas, given by different particles, one after another to a parabolic slit behind which was a Faraday cylinder. The relative abundance was given by measuring the total charge entering the cylinder during a standard interval of time, the conditions of the discharge being taken as constant. Dempster<sup>3</sup> used much the same device and was the first to obtain measurements of the relative abundances of isotopes by its means.

The writer<sup>4</sup> considered the possibility of applying the electrical charge method to the second mass spectrograph by an arrangement in which two Faraday cylinders collected the charges carried by the separate beams of two isotopic mass lines at the same time. This device eliminates the fundamental difficulty of obtaining a constant source, for the relative currents carried can be compared by a null method. This arrangement has quite recently been used with good results by Straus<sup>5</sup> for the analysis of nickel rays produced from a vacuum spark, but in 1929, for a variety of reasons, it was more convenient to continue to photograph the mass spectra and to work out a means of measuring abundance by photometry. Although for critical work on abundance the methods of photometry have now been entirely superseded by electrometric measurements they will be described in some detail in this chapter since more than a third of all the figures in the international table of abundances still depend on them.

**81. Photographic plates suitable for mass ray analysis.**—The earliest application of photographic plates to detect positive rays

<sup>1</sup> V. p. 207.

<sup>2</sup> J. J. Thomson, *Rays of Positive Electricity*, 2nd ed., 120, 1921.

<sup>3</sup> V. p. 70.

<sup>4</sup> Aston, *Proc. Roy. Soc., A*, 126, 511, 1930.

<sup>5</sup> *Phys. Rev.*, 59, 430, 1941.

has already been noted.<sup>1</sup> It was obvious from the first that their sensitivity to the rays bore little relation to their sensitivity to light. Sir J. J. Thomson realized that the penetrating power of the heavier rays was exceedingly small and that therefore the layer of sensitive silver salt should be as concentrated as possible. He endeavoured to make use of the old Daguerreotype process, which should give a maximum concentration, but without success. He records Schumann plates as being the most sensitive.<sup>2</sup>

Comparative tests made in 1919 convinced the writer that of plates then commercially obtainable the type known as "Paget Half Tone" were the most convenient. Although highly sensitive to the rays they may be manipulated in bright yellow light without fear of fog. They have an extremely fine grain and owing to the thinness of their sensitized layer are fixed, washed and dried much more rapidly than ordinary plates. By far the larger number of experiments on mass spectra up to 1932 were made with the aid of plates of this type.

In 1922 efforts were made to give these plates the extreme sensitivity of Schumann plates by removing the gelatine by a method similar to that of Ducleaux and Jeantet.<sup>3</sup> The sensitivity of the "schumannized" plates made in this way was not altered much for light high-speed rays, but for heavy ones it was greatly improved and led to the discovery of large numbers of new isotopes. Schumannized plates deteriorate rapidly on keeping and their preparation and use entail serious technical difficulties, an account of which was given in 1925.<sup>4</sup>

For the measurements of high accuracy performed with the second mass spectrograph uniformity was of paramount importance so that untreated Half Tone plates were used. Made with plate glass they were also used to develop the method of photometry to be described. During the latter work, however, an experimental type of Half Tone plate was tested.<sup>5</sup> These new plates, which for convenience were referred to as "Q" plates, were coated with a fast-process emulsion of low gelatine content and were prepared in one of the Ilford Company's laboratories. They are from 5 to 7 times as sensitive to mass rays as the commercial Half Tone plates. They possess all the good qualities of the latter with a steeper and longer linear log range and appear to be much the best plates for general and accurate quantitative work with the mass spectrograph.

These observations on plates refer to mass rays of energies ranging

<sup>1</sup> V. p. 23.      <sup>2</sup> *Rays of Positive Electricity*, 2nd ed., 4, 1921.

<sup>3</sup> Ducleaux and Jeantet, *J. Physique*, 2, 154, 1921.

<sup>4</sup> Aston, *Proc. Camb. Phil. Soc.*, 22, 548, 1925.

<sup>5</sup> Aston, *Proc. Roy. Soc.*, A, 132, 487, 1931.

from 20 to 50 kilovolts. The blackening of photographic plates by rays of energies in the region of 1 to 2 kilovolts has been studied quantitatively by Bainbridge<sup>1</sup> who gives curves for the opacity produced on Eastman X-Ray and Process plates by the impact of positive ions of the alkali metals. He comments on the extreme sensitivity of Schumann plates to rays of low velocity, but as they are unsuitable for photometry is unable to give any numerical data.

In order to link up his own observations with those of Bainbridge the writer has compared Q plates and Eastman X-Ray plates directly. Using rays of about 20 to 30 kilovolts energy it was found that Q plates were about 50 times as sensitive for heavy (mercury) rays and 250 times as sensitive for light (hydrogen) rays as Eastman X-Ray plates. A similar test of fresh Hilger Schumann plates showed that these might have a sensitivity as much as 20 times that of Q plates. The mass spectra illustrated in Plate VII were all obtained by Bainbridge with Schumann plates.

In January 1932, when the original batch of Q plates was finished, the writer started a systematic research in collaboration with Messrs. Ilford Ltd., with a view to evolving still better and more sensitive ones. Plates were coated with experimental emulsions in the Ilford Research Laboratory and then tested by the writer in a parabola apparatus set up in the Cavendish Laboratory for that particular purpose. This research proved long and laborious, and it was only in September 1934, after scores of emulsions had been tested that a great step forward was made and a plate produced which was estimated to be about 20 times as sensitive to heavy rays of about 30 kilovolts energy. These remarkable plates have been on the market ever since, and have been used in the great majority of the high accuracy doublet measurements described in Chapter X. Though slightly less sensitive to slow rays than Schumann plates they possess much greater uniformity which is so essential in work of this kind.

**82. Illusory photographic effects.**—In consequence of the very superficial nature of the effect of mass rays, the process of development in any photographic plates particularly sensitive to them will be so excessively rapid that uniformity in it is virtually impossible. In this way the form and apparent position of a line in too close proximity of another may be distorted, and the intensity of a weak line between two stronger ones drastically reduced. Misleading effects of this kind will obviously only occur when the resolving power of the instrument is inadequate.

There are two particularly interesting cases of such photographic illusions, one connected with the position and the other with the

<sup>1</sup> *J. Franklin Inst.*, 212, 489, 1931.

intensity of weak lines. They do not belong to the rank of major scientific chimeras, such as Blondlot's classic N-rays and Allison's recent Magneto-optic Method, creatures of the imagination which were only exorcised after a most deplorable waste of scientific effort, but they are worth recounting in some detail as a warning against the dictum "the camera cannot lie."

The first occurred during the original analysis of tin methyl, in the presence of xenon, with the first mass spectrograph in 1923. Particularly sensitive Schumannized plates were being used and a line at mass 135, quite correctly ascribed to  $^{120}\text{SnCH}_3$ , was observed to be lying unsymmetrically with regard to its neighbours 134 and 136 due to xenon. This appeared to prove beyond any doubt that in respect to the whole number rule tin and xenon must differ from each other by something like 2 parts in 1000. Theoretically this seemed preposterously unlikely, so the evidence, which appeared quite conclusive, was published<sup>1</sup> and the matter left till an instrument of higher resolving power became available. When the writer's second mass spectrograph was built, four years later, a further investigation of this interesting point was made with results illustrated in Plate VI, Spectrum X. The lines 134, 135, 136, now completely resolved, form a uniform series showing that the previous evidence was entirely misleading and due to the insufficient resolution of the lines.

The second case is concerned with the relative abundance of the two rare isotopes of nickel 61 and 64. In the first photometrical survey of mass spectra obtained from nickel carbonyl<sup>2</sup> both these lines were observed, but that at 64 grew weaker during the running and was therefore suspected to be partially, if not wholly, due to  $\text{SO}_2$  contamination, and so was not claimed as a certain isotope.

That this caution was unnecessary was shown shortly after by de Gier and Zeeman<sup>3</sup> analysing the carbonyl by the parabola method, who confirmed 64 to be a true isotope, but failed to detect 61 at all, though they admitted the difficulty of accounting for a line of this mass by contamination. Then Dempster<sup>4</sup> using a spark method eliminating possibility of contamination by compounds, and an instrument of very high resolving power, showed that 61 and 64 were both unquestionably true isotopes of, very roughly, equal abundance (*v. Plate IX*). Figures based on the writers photometric measurements, suitably adjusted in agreement with Dempster's results were adopted in the first International Table of Stable Isotopes for 1936.

<sup>1</sup> Aston, *Phil. Mag.*, **45**, 934, 1923.

<sup>2</sup> Aston, *Proc. Roy. Soc., A*, **149**, 396, 1935.

<sup>3</sup> *Proc. Roy. Acad. Amst.*, **38**, 810, 1935.

<sup>4</sup> *Phys. Rev.*, **50**, 98, 1936.

Recently the parabola analysis was repeated by Lub.<sup>1</sup> This time parabola 61 was detected, but its intensity estimated as *one-tenth* that of parabola 64. The beautiful photographs of the parabolas published, if accepted at their face value, were convincing enough, and appear to have deceived even experts, for Lub's figures were adopted in more than one unofficial table of isotopes. Not, however, in the international one for, warned by his experience related above, the writer re-examined his nickel spectra, and saw that on those least liable to contamination line 64 tended to be less intense than line 61, though the difference was not large, in good agreement with the more perfectly resolved ones of Dempster, and flatly contradicting the evidence of the parabolas.

The matter has fortunately now been put beyond controversy by electrical measurements of relative abundance, not involving photography at all. Straus,<sup>2</sup> and even more recently Valley,<sup>3</sup> both find that 61 is 1.3 times more abundant than 64. There seems little doubt that the explanation of this illusion is purely photographic, parabola 61 being starved in development by the too close proximity of the much more intense ones 60 and 62. Similar erroneous conclusions from parabolas in the cases of molybdenum and xenon are also probably due to insufficient resolving power.

**83. Methods of photometry.**—In 1929 the writer worked out methods by which the photographed spectra obtained with the second mass spectrograph could be used to provide measurements of the relative abundance of isotopes. These have been since applied to determine the isotopic constitution of a large number of elements.<sup>4</sup> Standard Paget Half Tone plates were used and to ensure the best photometry these were coated on plate glass. In order to get a reasonable range of intensity with rays which only affect the surface of the plate a very strong and rapid developer must be used. Hence no attempt was made to ensure absolute uniformity of development by elaborate thermostatic control and mechanical mixing devices. What was aimed at was a series of operations so simple that they could be repeated again and again without serious variation. 20 c.c. of the hydroquinone developer recommended by the makers was mixed in a strong glass boiling-tube the length of the plate and closed with a rubber bung. When the exposed plate had been removed from the mass spectrograph this developer was warmed, usually by the fingers, to 20° C. exact to about 0.05°. The plate was dropped

<sup>1</sup> Proc. Roy. Acad. Amst., 42, 253, 1939.

<sup>2</sup> Phys. Rev., 59, 102, 430, 1941.

<sup>3</sup> *ibid.*, 59, 836, 1941.

<sup>4</sup> Aston, Proc. Roy. Soc., A, 126, 511, 1930; 130, 303, 1931; 132, 487, 1931; 134, 571, 1932; 140, 535, 1933; 146, 46, 1934; 149, 396, 1935.

in and the tube was shaken longitudinally with considerable violence by hand for 90 seconds. The plate was then removed from the tube and rinsed in cold tap water for a few seconds after which it was fixed, washed and dried as usual. This period of development is rather less than that one would employ if searching for indications of the faintest lines, but it has the merit of leaving the background absolutely free from general fog and so simplifies the photometry. Comparisons are only made between lines on the same plate.

The measurements were made with a microphotometer by balancing the opacities against a standard wedge by a null method. The

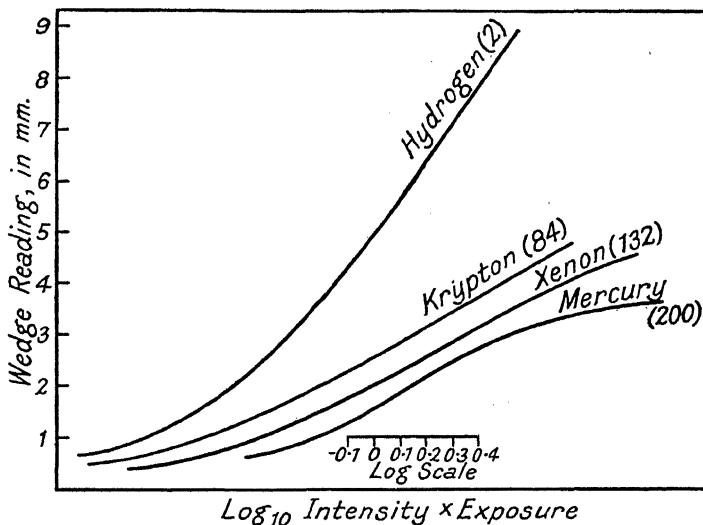


FIG. 24.—Curves illustrating the Photographic Effects of Mass Rays having the same Energy but different Mass. The Curves are only to be compared in general form, their positions relative to each other on the log scale have no significance.

opacity of mass spectrum lines on the plates used is generally low so that the instrument was fitted with a pair of Ilford wedges having the low contact density graduation of 0.39 per cm. Even with these the readings were usually less than 5 mm. For actual measurement it was decided to take the peak value read on the wedge, using a moderate slit width to give high sensitivity and to diminish the grain effect. The slit corresponded to 0.08 mm. on the surface of the plate.

The relation between the total quantity of rays deduced by methods to be described and the wedge readings of peak values is indicated by the curves shown in Fig. 24 which are plotted from results obtained with the hydrogen molecule and the atoms of krypton, xenon and mercury. The potential on the electric plates was 320 volts in each

case, corresponding to rays of about 38 kilovolts. The exact forms of the curves vary with every plate, but these are typical.

The effect of the different penetration is very clearly indicated. The highly penetrating hydrogen particles do not give a linear log law until a fair density has been reached, but after that the curve is linear and shows no sign of change of slope. The data for this curve are very rough. For the krypton more accurate figures are available. It is closely linear for a considerable range of wedge reading. Xenon has a shorter linear range and the slope of curve soon falls off. With mercury, which is the least penetrating of all, the increase in opacity falls off so soon that accurate deductions from wedge readings are only available over a very short range.

Having decided on the quantity to be measured, namely the peak values of the opacity of, say, two lines due to isotopes A and B, in order to connect it with the relative abundance of A and B we must make certain assumptions. The first and most important is that the ratio we wish to measure, the relative abundance of A and B, is a true invariant, and will be completely unaffected by experimental conditions. The evidence for this is overwhelming. The second assumption is that the photographic effect of A will be indistinguishable from that of B. This is approximate only, but since the masses of isotopes only differ by a few per cent. and their atoms have identical energies it is unlikely to lead to serious error in heavy elements. The third assumption is that the photographic effect will depend on the total number of particles striking the plate and not on the time they take to do so. In other words, with a constant source, if an exposure of R minutes with isotope B gives an effect identical with one of 1 minute with A we assume that the ratio of abundance of A to B is R. This is, of course, not strictly true of light quanta, but it seems sufficiently so for our purpose in the case of electrons and positive rays, and the results so far have justified its validity.

**84. Correction for position of lines.**—From the position of the plate in the mass spectrograph it is clear that the width of the lines will vary with their position, so that if peak values are used to measure intensities a correction will have to be applied when comparing lines some distance apart. In order to obtain a value for this the theoretical width of the image given by standard slits was worked out by a graphical method, perfect focusing being assumed, and plotted against the distance from the fiducial spot. The extreme variation was about 2 to 1 over the whole plate and was very nearly linear over the range employed. This variation is so similar to that of the dispersion factor that, to the accuracy expected of photometry, the relations between the actual line intensities of a group of isotopes may be treated as

constant over a reasonable range of the plate. The numerical correction is roughly 1·5 times the percentage difference in mass, e.g. the true relative abundance of  $^{86}\text{Kr}$  as compared with  $^{84}\text{Kr}$  will be 3·5 per cent. greater than that indicated by its line intensity derived from the peak value of opacity. Results indicate that imperfect focusing, which cannot be corrected for, gives rise to variations as great as those due to inequalities in the photographic emulsion, and there seems little doubt that really good measurements will only be obtained by taking account of the line as a whole by an electrical method. To do this photometrically seems impracticable.

**85. Method of intermittent exposures.**—The most formidable obstacle in the way of starting an investigation of the photometry of mass spectra is the problem of the constant source. Although, as will be seen, it is just possible, under particularly favourable conditions, to maintain a discharge approximately constant for several minutes, this is usually far from being the case, so that in the preliminary work it was essential that this source of uncertainty should be eliminated as far as possible. For this purpose two experimental conditions could be turned to advantage. The particular form of spherical discharge tube used was known to give very uniform distribution along the electric spectrum, and the resolution of the mass spectrograph was so high that a change in the electric field of  $\frac{1}{2}$  per cent. gave lines well separated. It was possible therefore to move a line to an independent position on the plate without serious alteration in its intensity.

The actual way this was applied is indicated in Fig. 25. G is a large wheel with its circumference accurately divided in degrees; it is fitted with two radial arms which can be set at any desired angle to each other. The wheel is rotated at a constant speed of about one revolution in 15 seconds by a gramophone motor. As the arms revolve they engage alternately with the rocking reversing switch  $S_1$ , which applies the potential of the cell C first in one direction and then in the other, through the potentiometer  $R_2$ , where it is reduced to a suitable small value, to the ends of the resistance  $R_1$  placed in the circuit maintaining the high potential on the + and - plates of the mass spectrograph. Hence instead of a single line at position corresponding to the standard voltage 320 volts we now get two lines, one each side of this position, near enough to be strictly comparable, peaks of which correspond to a ratio of exposures determined by the angle of the rotating arms. Changes in the condition of the discharge will have been minimized by breaking two long exposures into a very large number of intercalated ones. After one spectrum has been taken the hand switch  $S_2$  is reversed and an exactly similar one taken.

The mean value of these should, at least theoretically, eliminate the small change in intensity due to slightly different voltage.

In the first experiments the simpler arrangement shown on the right of the diagram was used. Here the rotating arms merely opened and closed the switch  $S$  which was tripped by hand after each spectrum had been completed. This gave reasonably consistent results, and as the changes in intensity with small alterations of potential could not be foretold exactly, and the random error due to the lack of uniformity in the photographic plate was large, it was only when work had proceeded for a long time that suspicion arose that the changes were not only greater than had been expected but not consistent.

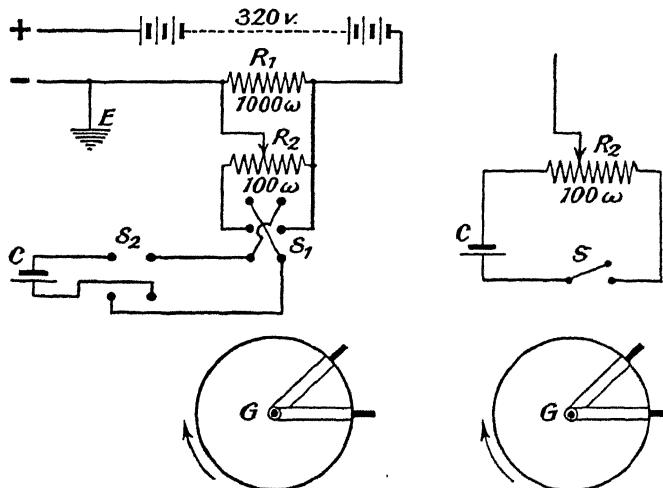


FIG. 25.—Diagram of connections used in the Method of Intermittent Exposures.

with the variations in the hardness of the discharge. A careful study of the lines under a lens then revealed the fact that those formed after make showed slightly but unmistakably different characters and shapes from those formed after break of the disturbing circuit. Earth shielding of the moving mechanism failed to remedy this, so one was driven to adopt the more complex but entirely symmetrical arrangement.

**86. Experiments with krypton.**—In the choice of an element for preliminary work one was guided by several considerations. It was essential that it should work well in the discharge tube. In order to make best use of the valuable fixed scale provided by nature it should have many isotopes with a large range of abundance. Finally its isotopes must differ by over 1 per cent. in mass so that the method of intermittent exposures could be applied. Krypton satisfies all

these conditions remarkably well. Its extreme rarity is no objection since the quantity used up is infinitesimal.

It is not necessary to describe the very large number of trials made with the arms of the rotating contact maker set at various ratios, 1 to 2, 1 to 3, 1 to 4, etc. It soon became evident that owing to the large random error due to inequalities in the surface of the photographic plate consistent numerical results could only be obtained by taking a mean of many spectra on the same plate. Six or seven were used as a rule. These indicated the range of opacity over which the log law could be trusted and enabled a curve such as that shown in Fig. 24 to be drawn. Such curves will not be identical for different plates but are of the same general form.

The measure of the fundamental ratio between the two strongest isotopes  $^{84}\text{Kr}$  and  $^{86}\text{Kr}$  was now undertaken by a method which virtually eliminates photometric error. Previous results showed that to obtain approximate equality between the reduced 84 line and the 86 line the contact angles would have to be set at 3.6 to 1. With this setting the mean of seven spectra showed a difference of only 0.02 mm. wedge reading. The effect of the penumbra of neighbouring lines had to be allowed for and this was done by plotting the contour of typical lines and calculating their stray effect at different distances. When this correction had been introduced it was found that the ratio of the intensities of the lines was 3.53. Several interpolations on the log curve of other spectra had given ratios approximating to this, and a very good plate of six spectra taken with ratio 2 to 1 gave a corrected log difference 0.547, an identical result. Taking 3.53 as the ratio of intensity of the lines and correcting for the different positions of the two lines on the plate we get at the final figure 3.41 for the relative abundance of these isotopes. This is probably within 2 or 3 per cent. of the true value.

The relative abundance of  $^{83}\text{Kr}$ ,  $^{82}\text{Kr}$  and  $^{80}\text{Kr}$  were then computed in a similar manner. That of the faintest isotope  $^{78}\text{Kr}$  could only be obtained very roughly. Table III gives the results obtained by photometry of krypton mass spectra :

TABLE III  
KRYPTON RESULTS<sup>1</sup>

Mass number of isotopes .	78	80	82	83	84	86
Log reciprocal line intensity	2.083	1.336	0.668	0.676	0	0.547
Relative abundance $^{84}\text{Kr} = 100$ . . . . .	0.74	4.31	20.75	20.75	100	29.37
Percentage abundance . .	0.42	2.45	11.79	11.79	56.85	16.70

<sup>1</sup> For the latest electrometric abundances see p. 157.

Knowing the masses of each isotope these figures enable the mean atomic weight on the physical scale to be fixed. As however the difference in packing fraction between isotopes is exceedingly small, sufficient accuracy is obtained by calculating the "mean mass number" 83.857 from the percentage composition and correcting this for the mean packing fraction which was then estimated to be — 8.8. This gave a mean atomic weight on the physical scale  $^{16}\text{O} = 16$  of 83.783. At that time the difference between this and the chemical scale was supposed to be 1 in 10,000 so that the chemical atomic weight of krypton was given as 83.77(5)  $\pm$  0.02 a value considerably higher than 82.92 deduced from density determinations and then in use.

**87. Experimental error.**—In evaluating the absolute ratio of abundance of isotopes the error may be of two kinds. One which may be called systematic is due to failure to fix the *scale* on which the ratios are measured through inconstancy of the source of error in timing. This clearly vanishes for lines of equal intensity and will be greatest when the ratio is high. The other is a purely random one due to inequality of the plate, focusing, etc., and will be just as high for equality as any other ratio. It is minimized by using the steepest part of the curve and can be reduced by taking a large number of observations. The photometer method is unfortunately very unsuitable for measuring large ratios of abundance. That between  $^{84}\text{Kr}$  and  $^{78}\text{Kr}$  has been arrived at by a series of ratios made possible by the occurrence of intermediate lines. The error is thus cumulative but even so the accuracy is far beyond any to be hoped for from a direct comparison of the lines.

In calculating atomic weights from mass spectra the matter takes on an entirely different aspect. Here we are interested in the position on the mass scale of the centre of gravity of the group of lines which may be termed the "mean mass number." The effect of the systematic error on this will disappear for any symmetrical group of lines, and the larger the number of isotopes present on each side of the mean the more their random errors may be expected to cancel. Hence the percentage error per unit of mass number will compare very favourably with that of the most accurate ratios of abundance, large errors in the abundance of rare isotopes being automatically compensated for by the very fact of that rarity. In order to estimate the probable error in atomic weight the effects due to abundance and position of each line have to be considered separately.

The experience obtained during the experiments on krypton was of great value in extending the work to other elements. In the case of heavy complex elements, such as tin and mercury, the method of intermittent exposures could not be used, for the resolution of the

apparatus was not sufficient. Instead the discharge was run as uniformly as possible and numerous exposures of different lengths made. From these, owing to the large number and range of abundance of the isotopes, it was possible to obtain calibration curves, as shown in Fig. 24, from which the best mean values could be deduced.

The determination of the values of the six main isotopes of mercury was of great importance. These form an approximate progression, a natural scale of abundance, and since the lines of this element appear on nearly all mass spectra obtained by the discharge tube they can be used as a comparison scale for obtaining fair values of abundance for any other elements, such as tungsten, osmium, etc., of approximately the same mass.

As a method of determination of chemical atomic weights photometry of mass spectra is clearly at its worst for light elements, for its error will be roughly a fixed fraction of the unit of mass. In addition with isotopes, as in lithium, so different in mass it is unsafe to conclude that particles of the same energy will affect the photographic plate equally. In the region of mercury the three sources of uncertainty due to packing fraction, change of scale and relative abundance have about the same value, each about 1 part in 10,000. Here the method will compare favourably with the best chemical ones and has obvious advantages from the fact that, in general, purity is of no importance, and the quantity of material required is usually only a fraction of a milligramme.

During systematic observations over a period 1930 to 1935 these methods of photometry were applied to some 58 elements including six different types of lead. In some 14 cases the atomic weights deduced showed serious discordances with the accepted chemical values. In these, with the single exception of tellurium<sup>1</sup> subsequent revisions supported the writer's mass spectrum values.

**88. Smythe and Mattauch's mass spectrometer.**—As has already been noted<sup>2</sup> an instrument, such as Dempster's shown in Fig. 5, which detects and measures beams of mass rays brought successively on to a fixed slit, may suitably be called a "Mass spectrometer." This term appears to have been first applied by Smythe and Mattauch to an instrument by which mass rays can be analysed without the use of magnetic fields. The analysis depends upon a special type of velocity filter described by Smythe in 1926.<sup>3</sup> The principle of this is that if the rays pass successively through two identical alternating fields all but those having certain velocities can be removed. These velocities can be selected by altering the distance apart and the frequency of the alternations, the distance apart of the centres of the fields being such

<sup>1</sup> V. p. 167.    <sup>2</sup> V. p. 38.    <sup>3</sup> Smythe, *Phys. Rev.*, 28, 1275, 1926.

that a particle having the specified velocity enters the second field when the phase is opposite to that in which it entered the first. Fig. 26 shows the first arrangement of the apparatus. Rays produced in a discharge tube emerge from the slit  $S_1$  and pass through the collimating slit  $S_2$  and then through the condensers forming the filter as indicated. The alternating field applied to the filter is supplied by a crystal-controlled oscillator with suitable amplifying system. The filtered beam is analysed by the deflecting electric field and peaks in the spectrum produced are detected by a collecting plate and electrometer at slit  $S_3$ .

Later<sup>1</sup> the deflecting field was modified according to the theory of Hughes and Rojansky<sup>2</sup> and the instrument used with noteworthy success to determine the abundance of the rare isotopes of oxygen. In actual working a number of unexpected effects were observed

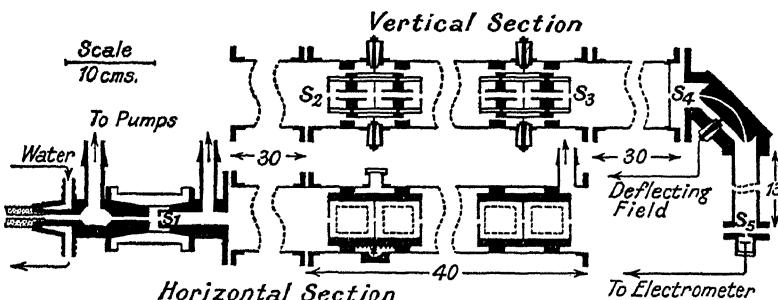


FIG. 26.—Diagram of the Mass Spectrometer.

giving rise, in particular, to numerous "ghosts." A full explanation of these interesting phenomena was later published by Hintersberger and Mattauch.<sup>3</sup>

**89. Nier's mass spectrometer.**—During recent years, owing largely to improved vacuum technique and the development of new methods of electrical measurement, mass spectrometry has rapidly advanced, especially in the United States of America. This advance is associated with such names as Bleakney, Brewer, Bluett, Sampson, Nier and others. The instruments used are generally modifications of the Dempster type, some were constructed for special purposes, such as the investigation of the cause of radioactivity in potassium and rubidium (q.v.), others for more general work. Among the latter a typical one of outstanding merit is that of Nier<sup>4</sup> which will now be described.

<sup>1</sup> Mattauch, *Phys. Zeit.*, **33**, 899, 1932.

<sup>2</sup> *Phys. Rev.*, **34**, 284, 1929.

<sup>3</sup> *Zeit. Phys.*, **106**, 279, 1937.

<sup>4</sup> *Phys. Rev.*, **52**, 933, 1937.

The analyser is of the simple semicircular focusing type shown in the scale diagram Fig. 27. Its most important feature is its construction of nichrome and copper parts which are completely housed in a pyrex glass container, and so can be effectively baked and outgassed when desired. This not only enables such very low pressures to be attained that quite moderate voltage rays can be used, but also secures the absolute exclusion of chance contamination which has always been such a bugbear in this work. The rays are formed by direct ionization of the vapour of the element concerned, or one of its compounds, by means of the tungsten filament F, and, as they pass the slits S<sub>1</sub>, S<sub>2</sub> are accelerated by suitable voltages applied to D, B and C, according to the theory of Bleakney.<sup>1</sup> Focusing on Slit S<sub>3</sub>, they are collected on plate P and measured by a valve amplifying device. The sensitivity

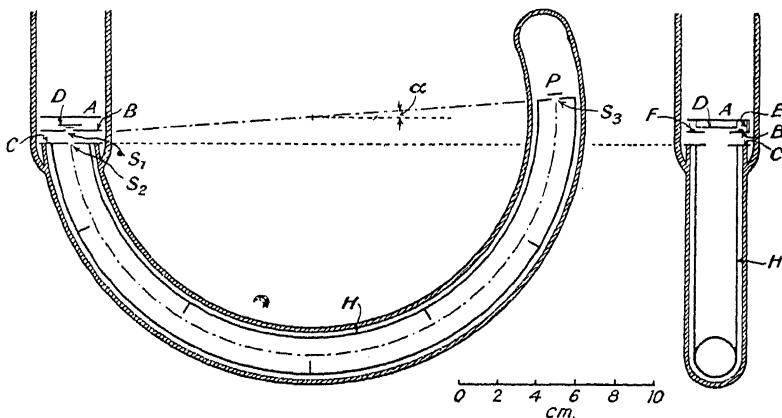


FIG. 27.—Diagram of Nier's Mass Spectrometer.

of the latter can be increased almost without limit so that abundances as low as 1 in 100,000 can be detected, which is particularly valuable in proving the absence of any particular mass number. To perform an analysis the analyser is placed between the poles of a large electromagnet the field of which is held constant to 1 in 10,000 by means of an ingenious automatic compensating device,<sup>2</sup> and the current plotted as the range of the accelerating voltage is swept over.

A typical curve, obtained with mercury, is shown in Figs. 28 and 29. The latter shows the region about mass number 196 plotted with greatly increased current amplification, and gives a good idea of the resolving power and sensitivity of the apparatus. The accuracy of measurement of normal ratios of abundance is claimed to be within

<sup>1</sup> Amer. Phys. Teacher, 4, 12, 1936.

<sup>2</sup> Nier, Rev. Sc. Instr., 6, 254, 1935.

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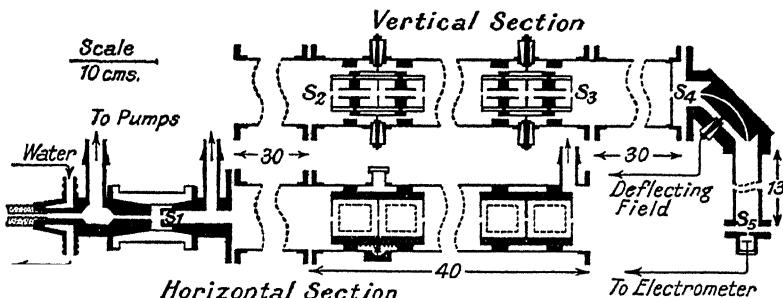


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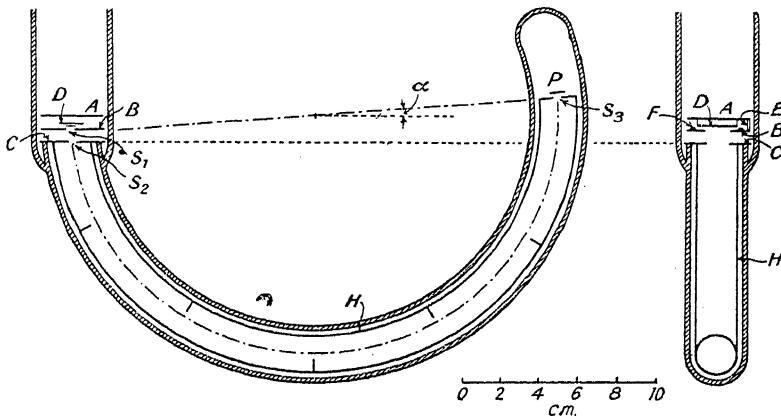


FIG. 27.—Diagram of Nier's Mass Spectrometer.

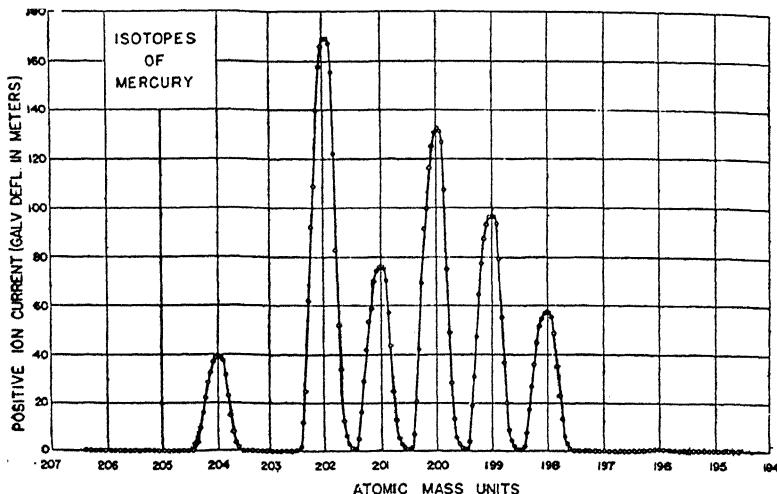
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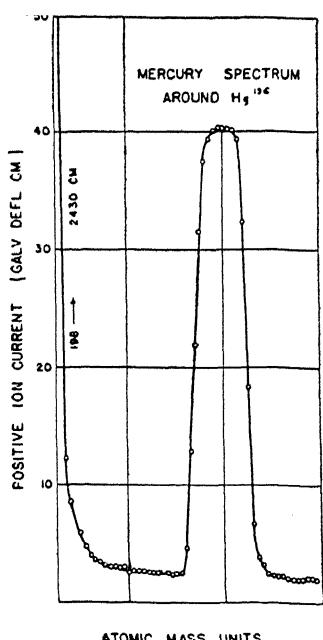
<sup>2</sup> Nier, Rev. Sc. Instr., 6, 254, 1935.

## MEASUREMENTS OF ABUNDANCE

FIG. 28.—Nier's Curve for Mercury.  $^{196}\text{Hg}$  just visible.

1 per cent., and in a brilliant series of researches, undertaken with the utmost attention to detail, Nier has provided data, quoted in Part III,

on a score or so of elements, which are the most reliable we have. In the course of this work new rare isotopes, such as those of osmium and sulphur, were found, and, what is of such outstanding importance in nuclear chemistry, the absence of certain mass numbers demonstrated to a quite unprecedented degree of refinement.

FIG. 29. — Mass Spectrometer of high sensitivity in region of  $^{196}\text{Hg}$ .

**90. Chemical analysis by the mass spectrometer.**—Sir J. J. Thomson in his book entitled *Rays of Positive Electricity and their application to Chemical Analysis*, first published in 1913, drew the attention of chemists to their new method of attack, and urged them to apply it to their practical problems. As a theoretical physicist unskilled in manipulation he did not realize the formidable experimental difficulties involved, and it was not till many years later, when these had been alleviated by improvements in vacuum and other techniques, that any progress was made. The first application of a purely chemical

nature appears to have been made by Conrad<sup>1</sup> who published plates of the beautiful groups of parabolas obtained from organic compounds and drew interesting conclusions from their appearance.

The immediate quantitative readings made possible by the use of valve amplifiers advanced the method enormously from the chemical point of view, and a modified Aston-type mass spectrometer so equipped was described by Taylor<sup>2</sup> who investigated the ionization of compound molecules by its means.

Quite recently the mass spectrometer has become a practical chemical tool of the greatest technical value, its most important applications being in the field of oil analysis.<sup>3</sup> It is found that when analysed by a higher power instrument of the Nier type, each hydrocarbon, methane, ethane—gives its own particular sequence of intensities of the various carbon groups of lines, called its "cracking pattern," and that this cracking pattern is different for normal and iso-butane for instance. From empirical knowledge it is possible, from the cracking pattern produced, to deduce the actual composition of a complex mixture of hydrocarbons. Its advocates claim that it is possible to run a qualitative and quantitative analysis of an unknown mixture of hydrocarbon gases, with an accuracy of better than plus or minus 5 per cent. of each of the various constituents. As this can be done in a short time, and requires only a minute sample, it will clearly be of fundamental importance in the petroleum industry.

<sup>1</sup> *Phys. Zeit.*, 31, 888, 1930.

<sup>2</sup> *Phys. Rev.*, 47, 666, 1935.

<sup>3</sup> Hoover and Washburn, *Petroleum Technology*, May, 1940.

## CHAPTER X

### MODERN HIGH-POWER MASS SPECTROGRAPHS

**91. Objects of high resolving power.**—The discovery of artificial disintegration in 1932, followed by that of neutron transmutation, led to a period of the greatest activity in nuclear physics. The demand for more and more accurate measurements of the masses of the nuclei concerned became imperative. For the purposes of nuclear theory the accuracy of 1 in 10,000, claimed in favourable cases for the writer's second mass spectrograph, was not only entirely inadequate, but the considerations of energy in the disintegration reactions indicated that in unfavourable ones, such as the indirect measurement of the oxygen helium ratio, the error was actually considerably greater.

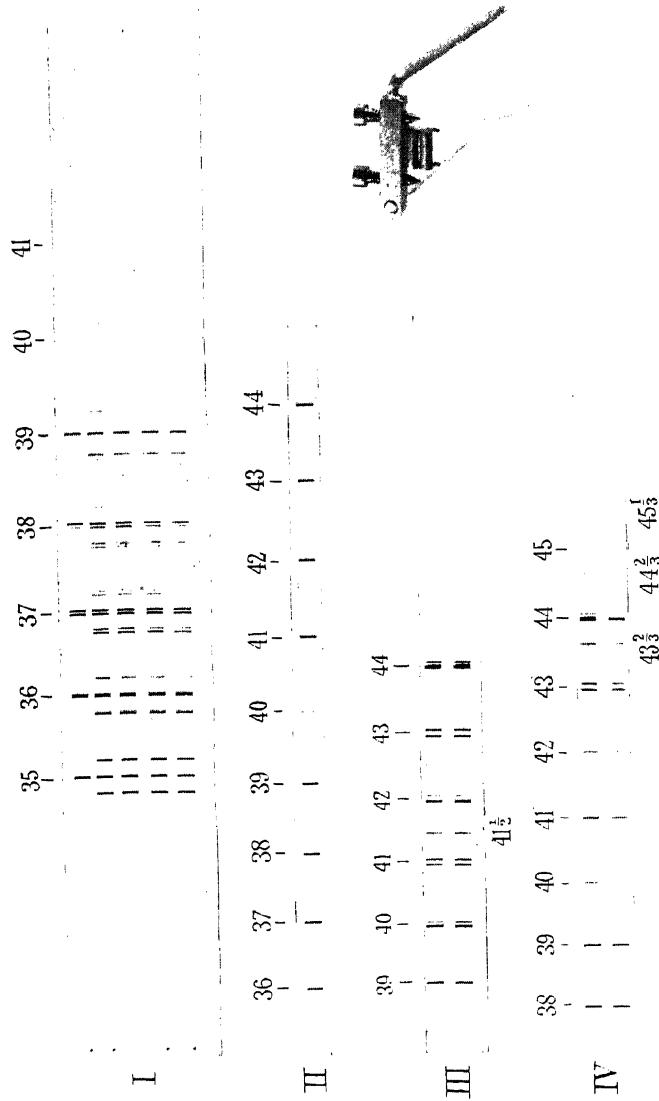
Fortunately during this period the discovery of deuterium supplied the one link required to enable the isotopic weights of light atoms to be compared with the standard oxygen by direct measurements of a series of natural doublets  $H_2 - D$ ,  $D_3 - C^{++}$ , and  $CH_4 - O$ . For the first and closest of these the work of Bainbridge<sup>1</sup> had shown that a resolving power of about 2000 would be required. For this purpose and for the accurate study of isotopic weights in general, a number of high-power instruments were designed and constructed, the more important of which will be described in this chapter. For convenience that of the writer will be considered first, since it embodies no fundamentally novel principle.

**92. Aston's third mass spectrograph.**<sup>2</sup>—In this instrument it was hoped to obtain the desired increase in accuracy and resolving power by improving the collimation and focusing of the rays. It was constructed in two stages. The collimator was formed of a brass tube at the ends of the axis of which were mounted two identical fine slits which define the beam. For the first time these were adjustable from outside as regards their effective aperture. The experimental device used is indicated in the photograph of one of these slits reproduced in Plate VIII. Two cylindrical metal wires 1 mm. thick are mounted exactly parallel and 0·05 mm. apart, so that they can be tilted with great delicacy about their midpoint by a long arm actuated through a ground

<sup>1</sup> V. p. 120.

<sup>2</sup> Aston, *Proc. Roy. Soc., A.*, **163**, 391, 1937.

PLATE VIII



### MASS SPECTRA OBTAINED WITH ASTON'S THIRD MASS SPECTROGRAPH; ADJUSTABLE SLIT (1937).



joint. As atomic diffraction was theoretically negligible it was hoped that this would act, for rays passing down the axis of the tube, practically as a slit whose aperture could be varied from 0.05 mm. to zero. Of course the continuous sharpening of the lines was expected to break down, even with theoretically perfect focusing, when the latter limit was approached, that it did so at a stage earlier than foreseen was probably due to the intense polarization of the metal surfaces under the action of the beam, and constituted the major disappointment in the performance of the apparatus.

The new collimator was tested by applying it to the existing mass spectrograph in place of the old one with fixed slits shown in Fig. 19. The resolving power was improved thereby enough to make a preliminary and partial resolution of the  $H_2 - D$  doublet.<sup>1</sup> Estimates of this and the other doublets concerned confirmed the conclusions from the observations on disintegration, that the masses of hydrogen and helium then in use were some 3 or 4 parts in 10,000 too low.

The next stage was to construct the main part of the instrument with dimensions such that second order focusing would be obtained. This problem had been worked out theoretically by Sawyer,<sup>2</sup> who showed that an electric

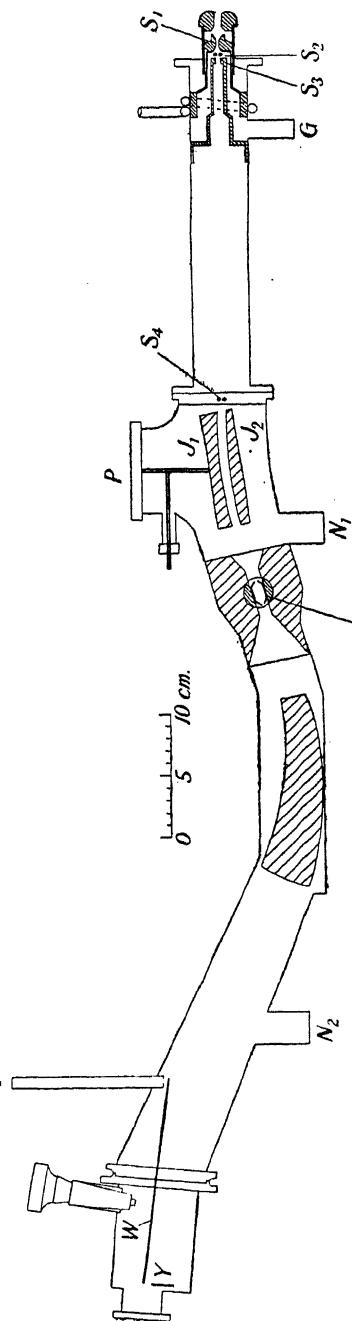


FIG. 30.—Diagram of Aston's Third Mass Spectrograph.

<sup>1</sup> *Nature*, **135**, 541, 1935.

<sup>2</sup> *Proc. Camb. Phil. Soc.*, **32**, 453, 1936.

deflection of a quarter of a radian in a radial field of radius 40 cm., followed by magnetic deflection by a uniform field between sickle-shaped sections of a circle of 15 cm. diameter would be favourable. The general construction is indicated in the scale diagram, Fig. 30.

A feature of this was that the electric deflecting plates  $J_1$ ,  $J_2$  could be easily removed to have their surfaces cleaned. As before the pole-pieces of the magnet were sickle-shaped, and a further refinement was the application of a very delicate fluxmeter control capable of detecting changes of the order of  $10^{-5}$  in the magnetic field. This field was stabilized by a spiral mercury resistance controlled by hand during the exposure.

**93. Performance of the instrument.**—In Plate VIII are shown some typical spectra produced. The scale is almost exactly linear as seen in Spectrum II. The dispersion coefficient, which was cali-

TABLE IV

## NATURAL DOUBLETS MEASURED (ASTON)

Mass no.	Doublet	Number of doublets measured	Difference in packing fraction	Difference in mass
2	$^1\text{H}_2$ - $^2\text{D}$	53	$7.54 \pm 0.2$	0.00152
4	$^2\text{D}_2$ - $^4\text{He}$	12	$63.5 \pm 0.2$	0.02551
6	$^2\text{D}_3$ - $^{12}\text{C}^{++}$	10	$70.3 \pm 0.3$	0.04236
10	$^{10}\text{B}$ - $^{20}\text{Ne}^{++}$	14	$16.83 \pm 0.15$	0.01684
14	$^{12}\text{C}$ $^1\text{H}_2$ - $^{14}\text{N}$	17	$8.89 \pm 0.05$	0.01245
16	$^{12}\text{C}$ $^1\text{H}_4$ - $^{16}\text{O}$	27	$22.48 \pm 0.1$	0.03601
(18)	$^{16}\text{O}$ $^1\text{H}_2$ - $^{36}\text{A}^{++}$	3	$15.09 \pm 0.2$	0.02711
(18)	$^{16}\text{O}$ $^1\text{H}_2$ - $^{18}\text{O}$	3	$5.80 \pm 0.1$	0.01044
19	$^{16}\text{O}$ $^2\text{D}$ $^1\text{H}$ - $^{19}\text{F}$	10	$9.64 \pm 0.15$	0.01833
20	$^{16}\text{O}$ $^2\text{D}_2$ - $^{20}\text{Ne}$	14	$15.41 \pm 0.2$	0.03083
20	$^{20}\text{Ne}$ - $^{40}\text{A}^{++}$	11	$5.44 \pm 0.15$	0.01088
24	$^{12}\text{C}_2$ - $^{48}\text{Ti}^{++}$	7	$10.20 \pm 0.15$	0.0479
26.4	$^{132}\text{Xe}^{++} + ^{-79}\text{Br}^{++}$	6	$28.30 \pm 0.3$	0.0745
(27)	$^{12}\text{C}_2$ $^1\text{H}_3$ - $^{27}\text{Al}$	2	$15.0$	0.0405
28	$^{12}\text{C}$ $^{16}\text{O}$ - $^{28}\text{Si}$	11	$6.15 \pm 0.2$	0.0172
29	$^{10}\text{B}$ $^{19}\text{F}$ - $^{29}\text{Si}$	7	$11.8 \pm 0.2$	0.0342
31	$^{12}\text{C}$ $^{19}\text{F}$ - $^{31}\text{P}$	18	$7.88 \pm 0.15$	0.0244
32	$^{16}\text{O}_2$ - $^{32}\text{S}$	18	$5.53 \pm 0.1$	0.0177
36	$^{12}\text{C}_3$ - $^{36}\text{A}$	6	$9.06 \pm 0.2$	0.0326
36	$^{12}\text{C}_3$ - $^1\text{H}$ $^{35}\text{Cl}$	8	$6.25 \pm 0.2$	0.0225
37	$^{12}\text{C}_3$ $^1\text{H}$ - $^{37}\text{Cl}$	22	$11.14 \pm 0.2$	0.0412
39	$^{12}\text{C}_3$ $^1\text{H}_3$ - $^{78}\text{Kr}^{++}$	4	$16.28 \pm 0.2$	0.0635
40	$^{12}\text{C}_3$ $^1\text{H}_4$ - $^{40}\text{A}$	10	$16.98 \pm 0.15$	0.0679
41	$^{12}\text{C}_3$ $^1\text{H}_5$ - $^{82}\text{Kr}^{++}$	19	$20.20 \pm 0.15$	0.0828
42	$^{12}\text{C}_3$ $^1\text{H}_6$ - $^{84}\text{Kr}^{++}$	20	$21.73 \pm 0.15$	0.0913
43	$^{12}\text{C}_3$ $^1\text{H}_7$ - $^{86}\text{Kr}^{++}$	18	$23.10 \pm 0.15$	0.0993
43	$^{12}\text{C}_3$ $^1\text{H}_7$ - $^{129}\text{Xe}^{++}$	14	$20.16 \pm 0.1$	0.0867
52	$\text{CH}_3$ $^{37}\text{Cl}$ - $^{52}\text{Cr}$	18	$9.22 \pm 0.15$	0.0479

brated by means of the twin bromine lines, was about 3 mm. for 1 per cent. difference in mass at one end of the plate, and 6 mm. at the other. The position of a line was estimated by a microphotometer to about 0.005 mm., which corresponds to about  $10^{-5}$  in mass, that is one-tenth of a unit of packing fraction. Actual measurements of doublets showed variations of an unexplainable nature considerably greater than this, and the lines themselves showed a curious structure. Tables IV and V contain the results obtained with this apparatus. The values of the packing fractions and isotopic weights deduced are given as published at the time. More reliable figures for these corrected by later values of the substandards will be given, under the elements concerned, in Part III.

TABLE V

## PACKING FRACTIONS AND ISOTOPIC WEIGHTS \* (ASTON)

Symbol	Packing fraction	Isotopic weight
$^1\text{H}$	+ 81.2	$1.00812 \pm 0.00004$
$^2\text{D}$	+ 73.55	$2.01471 \pm 0.00007$
$^4\text{He}$	+ 9.77	$4.00391 \pm 0.00016$
$^{10}\text{B}$	+ 16.1	$10.0161 \pm 0.0003$
$^{12}\text{C}$	+ 2.96	$12.00355 \pm 0.00015$
$^{14}\text{N}$	+ 5.28	$14.0073 \pm 0.0004$
$(^{18}\text{O})$	+ 3.2	$18.0057 \pm 0.0020$ )
$^{19}\text{F}$	+ 2.36	$19.0045 \pm 0.0005$
$^{20}\text{Ne}$	- 0.70	$19.9986 \pm 0.0006$
$(^{27}\text{Al})$	- 3.3	$26.9909$ )
$^{28}\text{Si}$	- 4.90	$27.9863 \pm 0.0007$
$^{29}\text{Si}$	- 4.7	$28.9864 \pm 0.0008$
$^{31}\text{P}$	- 5.30	$30.9836 \pm 0.0005$
$^{32}\text{S}$	- 5.53	$31.9823 \pm 0.0003$
$^{35}\text{Cl}$	- 5.71	$34.9800 \pm 0.0008$
$^{37}\text{Cl}$	- 6.10	$36.9775 \pm 0.0008$
$^{38}\text{Ar}$	- 6.10	$35.9780 \pm 0.0010$
$^{40}\text{Ar}$	- 6.15	$39.9754 \pm 0.0014$
$^{48}\text{Ti}$	- 7.24	$47.9652 \pm 0.0008$
$^{52}\text{Cr}$	- 8.18	$51.9575 \pm 0.0008$
$(^{58}\text{Ni})$	- 8.35	$57.9516 \pm 0.0020$ )
$(^{78}\text{Br})$	- 7.4	$78.9417 \pm 0.0020$ )
$(^{81}\text{Br})$	- 7.4	$80.9400 \pm 0.0020$ )
$^{78}\text{Kr}$	- 7.30	$77.9430 \pm 0.0020$
$^{82}\text{Kr}$	- 7.70	$81.9369 \pm 0.0015$
$^{84}\text{Kr}$	- 7.60	$83.9362 \pm 0.0015$
$^{86}\text{Kr}$	- 7.40	$85.9363 \pm 0.0015$
$(^{118}\text{Sn})$	- 5.8	$117.930$ )
$(^{120}\text{Sn})$	- 5.8	$119.930$ )
$^{129}\text{Xe}$	- 4.46	$128.9424 \pm 0.0020$
$(^{132}\text{Xe})$	- 4.4	$131.942$ )
$(^{200}\text{Hg})$	+ 1.4	$200.028$ )

\* Numbers in brackets, provisional.

**94. Principle of double focusing.**—In all the mass spectrographs so far described the beam of rays was made homogeneous in some respect before the focusing device was applied. Thus in Dempster's original apparatus the ion beam is of constant energy and is deflected and focused geometrically in a uniform magnetic field. In the writer's instruments, on the other hand, the beam is first rendered homogeneous geometrically by the use of a collimating device of two narrow slits, and then deflected and focused electromagnetically. In Bainbridge's system, and that of Smythe and Mattauch, a particular velocity is selected and then deflected and focused geometrically, in the first case by a uniform magnetic field, in the second by a radial electric field.

The next step was to examine if it was possible to arrange a system of electric and magnetic fields which would eliminate the necessity for collimation, and so produce the exact analogue of optical focusing of a single slit. As is so often the case in research, this principle, called "double focusing" received the attention of several investigators simultaneously and independently. A complete theory of all arrangements of a radial electric field and a homogeneous magnetic field for which both direction and velocity focusing can be obtained, was published by Hertzog and Mattauch and Hertzog,<sup>1</sup> and at the time these papers appeared, two mass spectrographs of entirely different design, but both making use of the principle, were actually in course of construction, by Dempster<sup>2</sup> in Chicago, and by Bainbridge and Jordan<sup>3</sup> in Harvard.

**95. Dempster's double focusing mass spectrograph.**—The general arrangement of this, the first double focusing instrument to give results is indicated in the diagram Fig. 31, which is taken from the paper cited above. In connection with it Dempster introduced an entirely novel source of ions, the "hot spark" between metal electrodes in a vacuum. This source, produced by a Tesla oscillating circuit, he had previously tested by the parabola analysis, and found to be particularly efficient in giving multiply charged ions. The ions so formed, are accelerated by a potential of 20 kilovolts between the slits S<sub>2</sub> and S<sub>3</sub>, as indicated, they are then deflected through 180 degrees by means of a radial electric field and a portion of the electric spectrum so produced is selected by an aperture S<sub>4</sub>. This beam is then deflected through a further 180 degrees by a magnetic field, and, for one particular radius, will come to a sharp focus on the photographic plate as shown. In this particular form of double focusing a perfect focus is given at one point only on the plate, and becomes less sharp as the distance from

<sup>1</sup> *Zeit. Phys.*, **89**, 447, 786, 1934.

<sup>2</sup> *Proc. Amer. Phil. Soc.*, **75**, 760, 1935.

<sup>3</sup> *Phys. Rev.*, **50**, 282, 1936.

this increases, but since the apparatus was designed for the analysis of the heavier elements, where the range of mass of the isotopes is small, and for the measurement of close doublets, this limitation, as Dempster points out, is of minor importance.

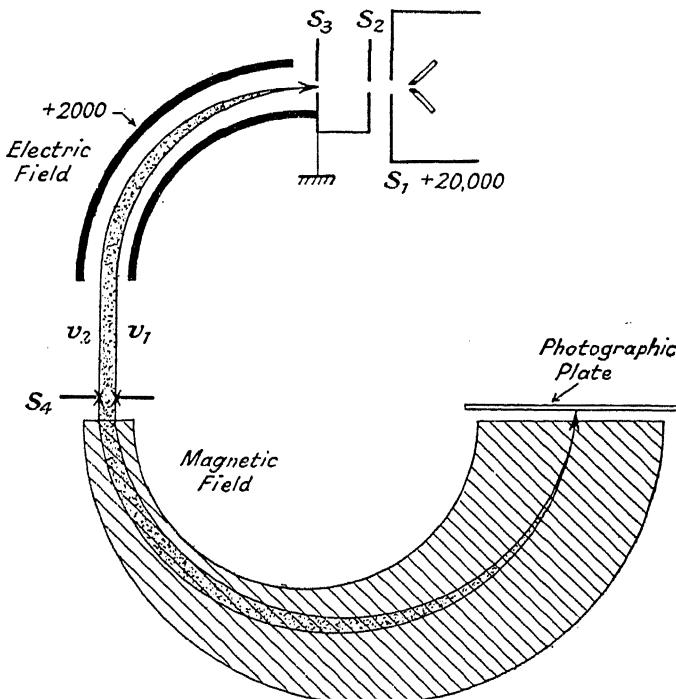


FIG. 31.—Diagram of Dempster's Double Focusing Mass Spectrograph.

**96. Experimental results.**—When Dempster's new apparatus was built, four elements, palladium, iridium, platinum and gold, remained to be analysed. The peculiar chemical properties of these elements had defeated all attempts to obtain their mass spectra, though some indications of the complexity of iridium was available from optical observations. With all four Dempster's spark method was brilliantly successful, yielding results which will be described in Part III. In addition to these important results a number of rare isotopes of other elements, particularly among the rare earths, were revealed for the first time. The mass spectrum of barium showing two very rare isotopes 130, 132 will be seen in Plate IX. Owing to the difficulty of obtaining a constant intensity in the beam, the spark method is not well adapted for the measurement of abundance, but quite recently, by the application of the device of two Faraday

cylinders<sup>1</sup> to Dempster's apparatus Straus<sup>2</sup> has succeeded in settling the controversial question of the relative abundance of the weak isotopes of nickel.<sup>3</sup>

**97. Dempster's packing fraction curve.**—A very valuable contribution to the subject made by Dempster is a large number of accurate measurements of the differences in packing fraction between elements. This he does in two different ways, either by measuring a natural doublet, such as  $^{16}\text{O}-^{18}\text{Ti}^{+++}$  shown in Plate IX, or by estimating the position of the line of one element between the lines of the other, such as  $^{27}\text{Al}$  between the lines of quadruply charged silver 107 and 109. To calibrate his plate he assumes that the difference in mass of the two

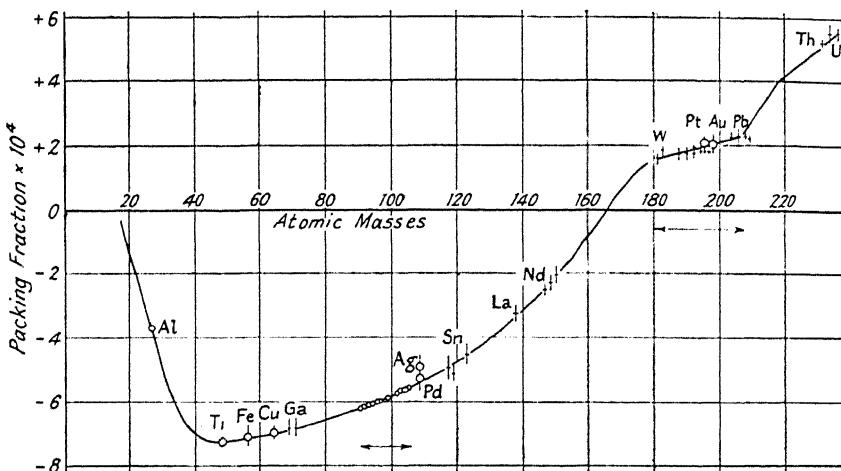


FIG. 32.—Dempster's Packing Fraction Curve (1938).

isotopes of one element, such as silver, is truly a whole number, an assumption which, among the heavy elements, is justified to the accuracy he claims.

Working on these lines he has constructed the very interesting packing fraction curve shown in Fig. 32 for the heavy elements. This shows that the original one on p. 81 is 1 to 3 units too low in this region, where it was known to be very rough. Table VI gives a summary of the differences of packing fraction measured with Dempster's apparatus<sup>4</sup> showing the ions compared.  $m$  indicates the position on the mass scale at which the measurement was made, and  $n$  the number of observations.

<sup>1</sup> V. p. 86.

<sup>2</sup> *Phys. Rev.*, 59, 102, 1941.

<sup>3</sup> V. p. 90.

<sup>4</sup> Dempster, *Phys. Rev.*, 53, 64, 869, 1938; Graves, *ibid.*, 55, 863, 1939.

TABLE VI  
PACKING FRACTION DIFFERENCES (DEMPSTER)

<i>m</i>	Ions compared	<i>n</i>	Difference
12	C 12-Ti 48	3	9.8 ± 0.4
14	N 14-Fe 56	8	12.3 ± 0.4
16	O 16-Ti 48	9	7.22 ± 0.1
16	O 16-Cu 63, 65	3	6.9 ± 0.2
19.5	Ru 99, 101-K 39	1	0.4 ± 0.3
20	Ru 99, 101-Ni 60	1	1.1 ± 0.3
21.3	Ag 107, 109-Zn 64	5	2.0 ± 0.3
22	Ag 107, 109-Zn 66	6	2.5 ± 0.3
23	Na 23-Zn 68, 70	2	4.9 ± 0.5
23.5	Sn 116, 118-Ti 47	5	2.23 ± 0.4
24.5	Sn 122, 124-Ti 49	2	2.73 ± 0.4
27	Al 27-Ag 107, 109	7	1.2 ± 0.2
27	Al 27-Pd 106	3	1.6 ± 0.3
39.4	Au 197-Sn 118, 119	5	7.2 ± 0.3
46.3	La 139-Ti 46, 47	5	2.23 ± 0.4
49	Nd 146, 148-Ti 49	9	4.60 ± 0.1
49.3	Nd 148-Ti 49, 50	9	4.79 ± 0.1
50	Nd 150-Ti 50	5	5.16 ± 0.1
52	Gd 156-Cr 52	18	6.37 ± 0.11
52	Gd 155, 157-Cr 52	16	6.39 ± 0.09
53	Gd 158, 160-Cr 53	10	6.38 ± 0.13
53.3	Gd 160-Cr 53, 54	6	6.33 ± 0.26
54	Ag 107, 109-Fe 54	2	2.55 ± 0.3
65	Pt 195-Cu 65	5	8.93 ± 0.1
65.6	Au 197-Cu 65	10	8.90 ± 0.2
69	Pd 102, 104-Ga 69	7	1.55 ± 0.2
71	Pd 106, 108-Ga 71	7	1.46 ± 0.2
86	Yb 172-Sr 86	24	6.20 ± 0.15
86	Yb 171, 173-Sr 86	13	6.48 ± 0.13
87	Yb 174-Sr 87	10	6.18 ± 0.14
87	Yb 173, Lu 175-Sr 87	7	6.37 ± 0.16
90.5	Ta 181-Zr 90, 91	6	7.71 ± 0.09
90.5	Ta 181-Zr 90, 92	6	7.77 ± 0.08
91	W 182-Zr 91	3	7.85 ± 0.2
92	W 184-Zr 92	3	8.05 ± 0.2
94	Os 188-Mo 94	1	7.78 ± 0.3
95	Os 190-Mo 95	1	7.76 ± 0.3
95.5	Ir 191-Mo 95, 96	9	7.68 ± 0.2
96	Ir 191, 193-Mo 96	9	7.72 ± 0.2
96	Os 192-Mo 96	1	7.58 ± 0.3
96	Os 192-Ru 96	19	7.65 ± 0.14
96	Os 190, Pt 194-Ru 96	5	7.70 ± 0.11
96	Os 192-Ru 96	3	7.91 ± 0.2
97	Pt 194-Mo 97	3	7.7 ± 0.2
97	Pt 194-Ru 96, 99	12	7.72 ± 0.17
97.5	Pt 195-Ru 96, 99	13	7.71 ± 0.20
98	Pt 196-Mo 98	4	7.68 ± 0.2
98	Pt 196-Ru 96, 99	12	7.69 ± 0.20
98.5	Au 197-Mo 98, 100	12	8.13 ± 0.07
99	Pt 198-Ru 99	26	7.92 ± 0.10
102	Pb 204-Pd 102	2	8.07 ± 0.2
102	Tl 203, 205-Pd 102	2	8.03 ± 0.2
103	Pb 206-Rh 103	3	7.96 ± 0.15
104	Pb 208-Pd 104	5	7.96 ± 0.15
104.5	Bi 209-Pd 104, 105	5	7.84 ± 0.1
116	Th 232-Sn 116	7	10.14 ± 0.1
117.5	U 235-Sn 117, 118	2	10.5 ± 0.3
119	U 238-Sn 119	26	10.12 ± 0.09
119	U 238-Sn 118, 120	14	10.12 ± 0.13
174	Yb 174-Yb 173, Lu 175	10	0.05 ± 0.20
175	Lu 175-Yb 173, 174	10	0.00 ± 0.34

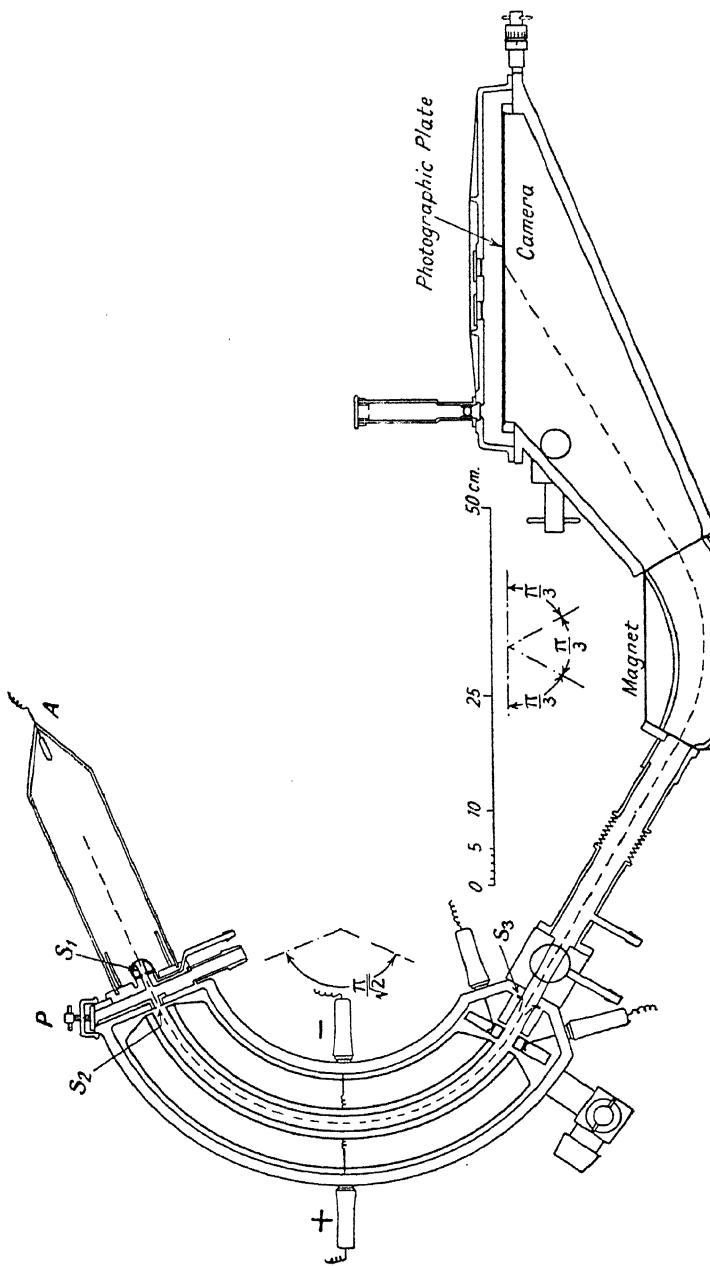


FIG. 33.—Diagram of Bainbridge and Jordan's Double Focusing Mass Spectrograph.

**98. Bainbridge and Jordan's double focusing mass spectrograph.**—In this instrument, a full account of which was first published in 1936,<sup>1</sup> double focusing is achieved by the arrangement shown in the accompanying diagram (Fig. 33). A beam of 20,000 volt mass rays, generated in a cylindrical discharge tube, passing through the narrow slit  $S_1$  and with its limits of divergence defined by a controlling slit  $S_2$ , is deflected by a radial electric field through Hughes and Rojansky's critical angle  $\frac{\pi}{\sqrt{2}}$ . A large potential of about 2,400 volts derived from radio batteries, is used on the deflecting plates, which are 1.9 cm. apart, so that the danger of polarizing effects, such as those described on p. 75, is much reduced. After further control by a variable slit  $S_3$ , the rays are next deflected through an angle  $\frac{\pi}{3}$  by a concentrated

magnetic field, and come to a focus on the photographic plate as indicated. For the full discussion of the paths of the rays, which gives linear displacement and good focusing over a 140-mm. spectrum, the reader is referred to the original paper.

**99. Performance of the instrument.**—The mean dispersion is 5 mm. for 1 per cent. difference of mass and the extremely sharp focus and high resolution achieved are indicated by the illustrations of enlarged doublets and the microphotometer record reproduced in Plate IX. One of the objects of the instrument was the search for rare and doubtful isotopes, particularly isobaric pairs, and by the use of wide slits and the recently improved Q plates this work was carried out very successfully. Lines in the mass spectra of Cd, Sn, Hg and Pb, previously thought to be isotopes, were shown to be spurious, but at least three isobaric pairs of odd mass numbers were confirmed beyond doubt.<sup>2</sup> Very valuable measurements of natural doublets made with this instrument have been published from time to time with increasing accuracy as the work proceeded, many of these will be noted in Part III. Tables VII and VIII of doublets and isotopic weights deduced from them is taken from Livingston and Bethe's review of the work.<sup>3</sup> A mass spectrograph of the Bainbridge and Jordan type has been recently constructed in Osaka University by Asada and his colleagues.<sup>4</sup>

**100. Mattauch's double focusing mass spectrograph.**—The first account of this very remarkable instrument was given by Mattauch in 1936.<sup>5</sup> It was constructed in Vienna in accordance with the theory of Mattauch and Hertzog,<sup>6</sup> already mentioned, and is unique in that it

<sup>1</sup> Bainbridge and Jordan, *ibid.*, **50**, 282, 1936.

<sup>2</sup> *V. p.* 205.

<sup>3</sup> *Rev. Mod. Phys.*, **9**, 370, 1937.

<sup>4</sup> *Nature*, **143**, 797, 1939.

<sup>5</sup> *Phys. Rev.*, **50**, 617, 1936.

<sup>6</sup> *Zeit. Phys.*, **89**, 786, 1934.

TABLE VII

## PACKING FRACTION DIFFERENCES (BAINBRIDGE AND JORDAN)

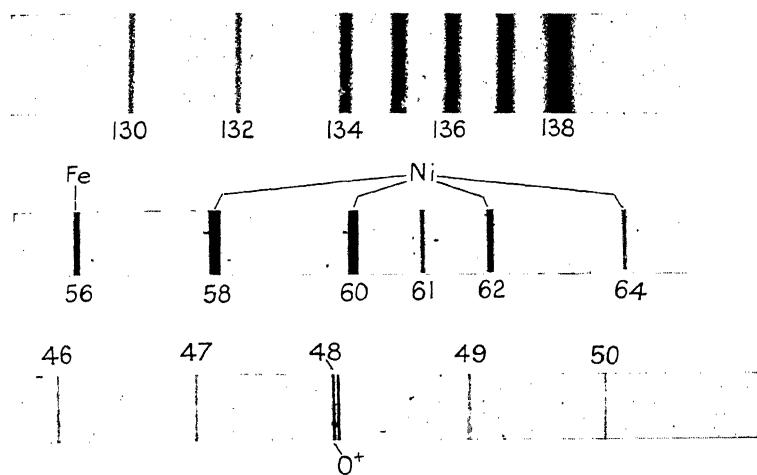
Mass number	Doubllets measured	Difference in $10^{-4}$ units
2	$^1\text{H}_2 - ^2\text{D}$	$15.3 \pm 0.4$
4	$^2\text{D}_2 - ^4\text{He}$	$256.1 \pm 0.4$
6	$^2\text{D}_3 - ^{12}\text{C}^{++}$	$421.9 \pm 0.5$
7	$^7\text{Li} - ^{14}\text{N}^{++}$	$144.3 \pm 1$
8	$^4\text{He}_2 - ^{16}\text{O}^{++}$	$77.2 \pm 1.2$
10	$^{10}\text{B} - ^{20}\text{Ne}^{++}$	$167.5 \pm 1.5$
10	$^9\text{Be}^1\text{H} - ^{10}\text{B}$	$69.6 \pm 2$
10	$^9\text{Be}^1\text{H} - ^{20}\text{Ne}^{++}$	$239.1 \pm 2$
11	$^{10}\text{B}^1\text{H} - ^{11}\text{B}$	$116.0 \pm 1$
11	$^{10}\text{B}^1\text{H} - ^{22}\text{Ne}^{++}$	$251 \pm 5$
11	$^{11}\text{B} - ^{22}\text{Ne}^{++}$	$136.0 \pm 1.5$
12	$^{10}\text{B}^1\text{H}_2 - ^{12}\text{C}$	$287.5 \pm 2$
12	$^{11}\text{B}^1\text{H} - ^{12}\text{C}$	$171.4 \pm 1$
13	$^{12}\text{C}^1\text{H} - ^{13}\text{C}$	$45 \pm 1$
14	$^{12}\text{C}^1\text{H}_2 - ^{14}\text{N}$	$127.4 \pm 0.8$
15	$^{14}\text{N}^1\text{H} - ^{15}\text{N}$	$107.4 \pm 2$
16	$^{12}\text{C}^1\text{H}_4 - ^{16}\text{O}$	$364.9 \pm 0.8$
16	$^{14}\text{N}^1\text{H}_2 - ^{16}\text{O}$	$236.9 \pm 1.5$
20	$^{16}\text{O}^2\text{D}_2 - ^{20}\text{Ne}$	$306.5 \pm 1$
20	$^{20}\text{Ne} - ^{40}\text{A}^{++}$	$113.0 \pm 2$
20	$^{16}\text{O}^2\text{D}_2 - ^{40}\text{A}^{++}$	$418.9 \pm 2$
21	$^{20}\text{Ne}^1\text{H} - ^{21}\text{Ne}$	$72.6 \pm 2$
28	$^{14}\text{N}_2 - ^{12}\text{C}^{16}\text{O}$	$111.7 \pm 2$

TABLE VIII

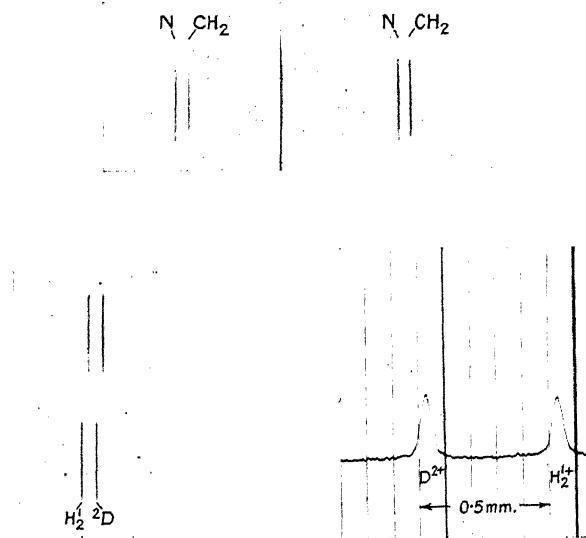
## ISOTOPIC WEIGHTS DEDUCED (BAINBRIDGE AND JORDAN)

$^1\text{H}$	$1.00813 \pm 0.000017$	$^{12}\text{C}$	$12.00398 \pm 0.00009$
$^2\text{D}$	$2.01473 \pm 0.00002$	$^{13}\text{C}$	$13.00761 \pm 0.00015$
$^4\text{He}$	$4.00389 \pm 0.00007$	$^{14}\text{N}$	$14.00750 \pm 0.00008$
$^7\text{Li}$	$7.01818 \pm 0.00012$	$^{15}\text{N}$	$15.00489 \pm 0.0002$
$^9\text{Be}$	$9.01516 \pm 0.0002$	$^{20}\text{Ne}$	$19.99881 \pm 0.00011$
$^{10}\text{B}$	$10.01631 \pm 0.00020$	$^{22}\text{Ne}$	$21.99864 \pm 0.00036$
$^{11}\text{B}$	$11.01292 \pm 0.00016$	$^{40}\text{A}$	$39.97504 \pm 0.00026$

gives theoretically perfect double focusing along the whole length of the plate. As shown in the diagram Fig. 34, the sequence of the fields is similar to that in the first mass spectrograph, but the position of the magnetic field in respect to the plate quite different. A pencil of rays emerging from the fine slit S is deflected by a radial electric field through an angle  $\frac{\pi}{8}$ . It then passes through the controlling diaphragm B and is deflected in the opposite direction, through a right angle, between the pole-pieces of a large electromagnet, shaped as shown, to focus on a photographic plate which lies on the edge of the magnet. This plate is no less than 298 mm. long, and the claim that absolutely sharp focus is obtained from end to end of this is strikingly justified by

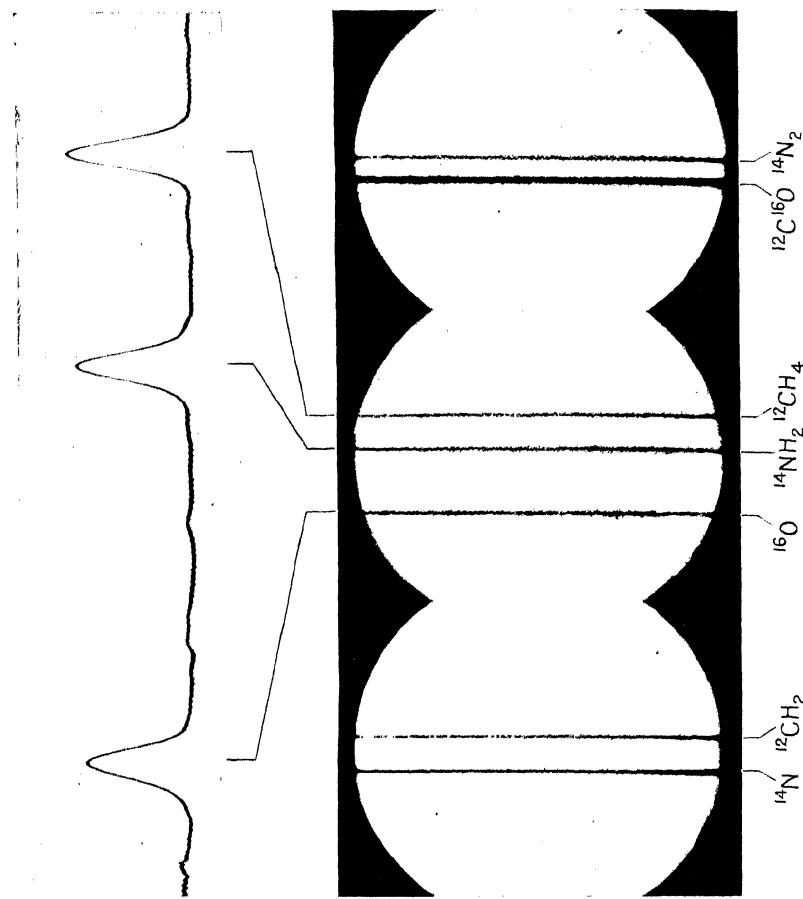
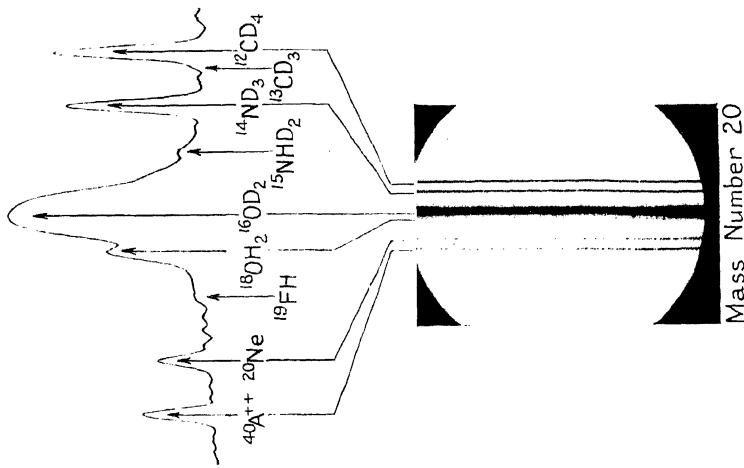


MASS SPECTRA OBTAINED BY DEMPSTER (1936, 1937).



DOUBLETS AND PHOTOMETER TRACES, BAINBRIDGE AND JORDAN (1936).

PLATE X



DIFFERENT AND FINE STRUCTURE, MATTAUCh (1938).

the reproductions of entire spectra published.<sup>1</sup> The displacement follows a square root law exactly, and masses ranging from 1 to 10 can be recorded simultaneously over three octaves of mass, an enormous range compared with that of other instruments. As is implied by this the dispersion coefficient is comparatively small from 0·35 to 1·8 mm. for 1 per cent. difference of mass, but for doublet measurement of high precision this is offset by the almost incredible sharpness of the lines obtained with Q plates, the relative position of which is estimated to about 0·0003 mm. This is well illustrated in Plate X where the lines, very much enlarged, are shown with photometer traces to correspond.

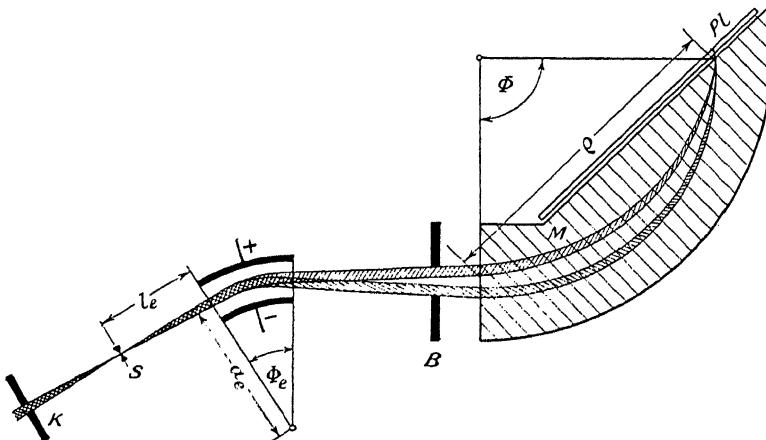


FIG. 34.—Diagram of Mattauch's Double Focusing Mass Spectrograph.

These results were published in 1938, after many detail improvements in the apparatus had been made.<sup>2</sup> By measuring the same doublet at many different points, over a very wide range of dispersion, Mattauch ensures results of great reliability. Tables IX and X show his 1938 figures for a number of doublets, and for the isotopic weights deduced. His latest 1940 estimates for the substandards are given on p. 116.

In addition to the precision mass measurements Mattauch has turned his double focusing instrument to a great variety of important researches. As already noted one of them is the investigation of numerous bands.<sup>3</sup> By photometry he has estimated the isotopic abundance of many elements including molybdenum, europium and lutecium, in which he discovered the new isotope 176 and a variety of common and radiogenic leads. His outstanding work on radiogenic strontium is described on p. 159 and illustrated in Plate XI, p. 234.

<sup>1</sup> *Sitz. Akad. Wien.*, **145**, 461, 1936.

<sup>2</sup> Mattauch, *Zeit. tech. Phys.*, **12**, 578, 1938.

<sup>3</sup> V. p. 63.

TABLE IX

## PACKING FRACTION DIFFERENCES (MATTAUCh)

Mass number	Doublts measured	Difference in $10^{-4}$ units
4	$^1\text{H}_2-^2\text{D}$	$15.39 \pm 0.021$
6	$^2\text{D}_3-^{12}\text{C}^{++}$	$422.39 \pm 0.21$
14	$^{12}\text{CH}_2-^{14}\text{N}$	$125.81 \pm 0.23$
15	$^{12}\text{C}^1\text{H}_3-^{15}\text{N}$	$238.2 \pm 0.8$
15	$^{12}\text{C}^1\text{H}_3-^{14}\text{N}^1\text{H}$	$125.63 \pm 0.27$
16	$^{12}\text{C}^1\text{H}_4-^{18}\text{O}$	$364.06 \pm 0.40$
16	$^{14}\text{N}^1\text{H}_2-^{18}\text{O}$	$237.80 \pm 0.32$
17	$^{14}\text{N}^1\text{H}_3-^{18}\text{O}^1\text{H}$	$236.61 \pm 0.39$
18	$^{16}\text{O}^1\text{H}_2-^{18}\text{O}$	$125.7 \pm 1.8$
20	$^{12}\text{C}^2\text{D}_4-^{20}\text{Ne}$	$638.16 \pm 0.50$
20	$^{20}\text{Ne}-^{40}\text{A}^{++}$	$111.42 \pm 0.38$
28	$^{14}\text{N}_2-^{12}\text{C}^{16}\text{O}$	$112.22 \pm 0.40$

TABLE X

## ISOTOPIC WEIGHTS DEDUCED (MATTAUCh)

$^1\text{H}$	$1.008132 \pm 0.0000038$
$^2\text{D}$	$2.014726 \pm 0.0000074$
$^{12}\text{C}$	$12.00387 \pm 60.000032$
$^{14}\text{N}$	$14.00756 \pm 0.000040$
$^{18}\text{O}$	$18.0037 \pm 0.0007$
$^{20}\text{Ne}$	$19.99896 \pm 0.000066$
$^{40}\text{A}$	$39.97564 \pm 0.000153$

**101. Jordan's high dispersion mass spectrograph.**—Recently results with a new instrument have been announced by Jordan.<sup>1</sup> This has a dispersion coefficient of 14.6 mm. for 1 per cent. difference of mass, and a resolving power 30,000, far the greatest up to date. No full description is available, but it uses velocity selection in addition to double focusing. By its means a large number of measurements of the  $\text{CH}_2-\text{N}$  doublet have been made with a mean result of  $125.6 \pm 0.15 \times 10^{-4}$  units. This corresponds to an accuracy of about one in a million. The following figures, which are only very rough, give some idea of the increase in power of mass spectrographs built during the past twenty-one years.

	Date	Mean Dispersion	Resolving Power	Accuracy
Aston I . . . . .	1919	1.1	130	$10^3$
Aston II . . . . .	1925	2.2	600	$10^4$
Bainbridge . . . . .	1930	2.7	600	$10^4$
Dempster . . . . .	1935	1	1000	$10^4$
Bainbridge and Jordan	1936	5	10,000	$10^6$
Aston III . . . . .	1936	5	2000	$10^6$
Mattauch . . . . .	1937	1.4	6500	$10^6$
Okuda . . . . .	1939	4.6	17,000	$10^6$
Jordan. . . . .	1940	14.6	30,000	$10^6$

**102. Isotopic weights by the doublet method.**—As has already been pointed out,<sup>1</sup> the highest accuracy of measurements of mass can only be attained with lines close together and of equal intensity. At the time this was urged practically only one such natural doublet that of CH<sub>4</sub>–O, had been resolved and measured, but it was foreseen that the most interesting structure of, for instance, line 28, due to Si, CO, N<sub>2</sub>, C<sub>2</sub>H<sub>4</sub>, etc., was to be expected once the necessary resolving power was available. It was realized that the lines of the hydrocarbons would provide a valuable series of natural standards of mass, but it could not then be foreseen that the masses of hydrogen and carbon could be linked to that of the standard oxygen by natural doublets. This was only made possible by the discovery of deuterium in 1932, with its atom directly comparable with the molecule of hydrogen on the one hand, and its triatomic molecule with the doubly charged atom of carbon on the other. The three fundamental doublets connecting the four atoms are clearly H<sub>2</sub>–D at mass 2, D<sub>3</sub>–C<sup>++</sup> at mass 6, and CH<sub>4</sub>–O at mass 16. Once values for these are obtained, in the form of mass differences, the isotopic weights in terms of <sup>16</sup>O can be calculated quite simply. Some of the numerous measurements of these, and of the CH<sub>2</sub>–N doublet at 14, are given in the following table. The mass differences are expressed in 10<sup>-4</sup> units on the physical scale of isotopic weight <sup>16</sup>O = 16. With regard to order, whether we should write the lighter or the heavier component of a doublet first is purely a matter of convention. In published reproductions of mass spectra the masses usually increase from left to right, so the first alternative seemed natural, and was used by the writer in the past. On the other hand, putting the heavier first has the advantage that it allows the dash to function as a negative sign. This is now generally adopted.

TABLE XI  
FUNDAMENTAL DOUBLETS  
Differences of Mass expressed in 10<sup>-4</sup> units

Observer	H <sub>2</sub> –D	D <sub>3</sub> –C	CH <sub>4</sub> –O	CH <sub>2</sub> –N
Aston '27 . . .			350	
Aston '35 . . .	14.2	419.5	374	
Aston '36 . . .	15.2 ± 0.4	423.6 ± 1.8	360.1 ± 2.4	124.5 ± 0.7
B. and J. '36 . . .	15.3 ± 0.4		369 ± 2	130 ± 2
M. '37 . . .			366.9 ± 0.6	124.3 ± 0.3
B. and J. '37 . . .			364.9 ± 0.8	128.0 ± 0.6
M. '38 . . .	15.39	421.9 ± 0.5	364.06	127.4 ± 0.8
	± 0.021	422.39	± 0.40	125.81
Okuda '39 . . .		± 0.21	364.2 ± 0.9	125.7 ± 0.6
Jordan '40 . . .				125.6 ± 0.15

<sup>1</sup> V. p. 76.

## 116 MODERN HIGH-POWER MASS SPECTROGRAPHS

The discordance between the 1936 values for the CH<sub>4</sub>-O doublet obtained by the precision instruments of Bainbridge and Jordan, and that of the writer, will be noticed, and later values converging on an intermediate one make it quite clear that the writer's value for <sup>12</sup>C, although apparently supported by less direct measurements<sup>1</sup> is, in fact, too low by about 1 in 40,000.

The latest figures for the isotopic weights assigned by Mattauch<sup>2</sup> to the most important substandards are :

<sup>1</sup> H	1.008130	± 0.0000033
<sup>2</sup> D	2.014722	± 0.0000064
<sup>12</sup> C	12.003861	± 0.000024

which are adopted in this book. The large excess mass of H and D is most convenient technically, for it results in the doublets provided by ordinary and "heavy" hydrocarbon molecules with the atoms of the elements being wide enough for easy resolution, as shown in the case of krypton and zenon in Plate VIII.

<sup>1</sup> *Nature*, **139**, 922, 1937; **143**, 797, 1939.

<sup>2</sup> *Phys. Rev.*, **57**, 1155, 1940.

## PART III

### THE ELEMENTS AND THEIR ISOTOPES

#### CHAPTER XI

**Introduction.**—In this part of the book the results obtained by the experimental methods described in Parts I and II are summarized for all the elements, taken in the natural order of atomic number. As there is no sharp natural boundary between stable and unstable isotopes the limitations are artificial and dictated mainly by convenience. The unstable products of artificial transmutation are omitted entirely, and naturally radioactive bodies and their products are only considered when available in quantities sufficient for mass spectrum analysis. This account constitutes a summary with references, of all the data upon which have been based the first International Table of Stable Isotopes in 1936 and each of its annual publications since. In conformity with these tables the relative abundances of the isotopes of complex elements is generally stated in percentage form, though when two isotopes only are present the more convenient ratio is used. Many workers express their abundance results for complex elements as ratios, the abundance of the predominant isotope being taken as 100. This practice has some obvious advantages, particularly when dealing with the introduction of new rare isotopes, but after careful consideration the percentage method was adopted by the committee concerned.

As regards measurements of mass no international table of values has yet been decided upon. The data in the form of packing fractions and isotopic weights, on the physical scale  $^{16}\text{O} = 16$ , is reviewed here as published. Where substandards are involved Mattauch's figures quoted on p. 116 are used in the calculations. For the evaluation of chemical atomic weights of the elements the ratio, now internationally accepted, between the physical and chemical scales, of 1.000275 will be used.

##### *1. Hydrogen.*

Hydrogen, the lightest of all chemical elements, has naturally played a predominant part in the development of mass spectrum analysis. Derived from the water in the glass walls of the tube, and from other

## I. HYDROGEN

compounds, it is invariably present in the normal discharge, and the effects of its atom and molecule on the fluorescent screen were in fact the first phenomena observed in positive ray analysis. Since, with beams of ordinary intensity, these two bodies are the only ones giving fluorescent effects easily discernible visually, they are, and are likely to remain, of indispensable value in testing and developing apparatus for analysis.<sup>1</sup> It is hardly necessary to state that no positively charged particle has been observed of smaller mass than the hydrogen atom, though a band effect may be produced at mass 0·5 which is due to abnormal conditions.<sup>2</sup>

Hydrogen behaves in the discharge like an electronegative element in that its nucleus tends to capture two electrons to form a negatively charged atomic ray  $H^-$ . The parabola due to negatively charged hydrogen will be clearly seen in Plate I.

Two positively charged molecules  $H_2$  and  $H_3$  usually occur, but in very disproportionate degree. The former gives the brightest line found in the ordinary low-pressure discharge, but the latter is usually barely distinguishable. Sir J. J. Thomson discovered that gas rich in  $H_3$  could be produced by bombarding certain substances, such as solid KOH, with cathode rays.

At the outset from the most general considerations, in spite of its fractional atomic weight, it appeared extremely improbable that hydrogen was a complex element, for the whole number rule would imply a difference of 100 per cent., at least, in mass for a possible heavier constituent. When, as expected from theory, it was demonstrated in 1920<sup>3</sup> that the mass of the hydrogen atom did in fact exceed a whole number by the amount assigned by chemists, all doubt seemed virtually at an end and hydrogen was confidently announced to be a simple element. The story of how this came to be disproved, years later, by the discovery of "heavy hydrogen" is one of the most interesting in modern science, abounding, as it does, in the unexpected and paradoxical.

In 1925 Costa had repeated the writer's bracketing experiments with greater precision, and had arrived at the value 1·0079 for the weight of the hydrogen atom. Shortly after still more accurate determinations were made during the writer's first survey of the packing fractions with his second mass spectrograph.<sup>4</sup>

The hydrogen molecule was compared with the helium atom by Method III<sup>5</sup> and measured against the known ratio  $H : H_2$ . The voltages applied were approximately in the ratio 2 : 1·004, so that the  $H_2$  line was on the heavy side of each doublet. The difference between

<sup>1</sup> V. p. 45.

<sup>2</sup> V. p. 61.

<sup>3</sup> V. p. 51.

<sup>4</sup> Aston, *Proc. Roy. Soc., A*, 115, 502, 1927.

<sup>5</sup> V. p. 79.

the packing fractions of hydrogen and helium is the sum of the two intervals corrected for the mass of the electron. The intervals of mass came out on three plates to be 73.7, 73.6, 73.9, mean 73.73. From this must be subtracted the correction for the electron which in this particular case amounts to  $\frac{1}{4} m_0 = 1.35 \times 10^{-4}$ , whence we get 72.4 as the excess of the packing fraction of hydrogen over that of helium. This figure we now know to be well within the limits of accuracy, one unit, then claimed. It was obtained under good experimental conditions, and was practically identically confirmed by Bainbridge's<sup>1</sup> direct measurements of the doublet, H<sub>2</sub>-He made six years later and reproduced in Plate VII. The packing fraction of helium,<sup>2</sup> measured with much greater difficulty, was estimated at 5.4, a value now known to be much too low. The sum gave the packing fraction of hydrogen to be 77.8 and therefore its isotopic weight to be 1.00778, a value identical with the best determinations of its atomic weight. The packing fractions of carbon and nitrogen, both believed to be simple, also agreed very exactly with the chemical data.

This concordance, regarded at the time as highly satisfactory, was completely upset in 1929 by the unexpected discovery of the heavier isotopes of oxygen. It was soon proved that the abundance of these involved a change of scale of at least two units of packing fraction, and by an almost incredible coincidence, similar heavier constituents of carbon and nitrogen were revealed in quantity just about enough to give the corresponding shift of their atomic weights.

At that time the chemical atomic weight of hydrogen was regarded as completely trustworthy, and one of the most accurately determined natural constants. It was given as  $1.00777 \pm 0.00002$  by Birge<sup>3</sup> in 1930 who later, with Menzel,<sup>4</sup> pointed out that to bring the results of the mass spectrograph and those of the chemists into accord hydrogen must contain heavier isotopes. Fortunately unaware that, as we now know, the error in each of the estimates concerned was greater than the total discrepancy he was seeking to explain, Urey started his famous painstaking search which resulted in the remarkable discovery of heavy hydrogen, and for which he received the well deserved award of the Nobel Prize in 1934.

With Brickwedde and Murphy<sup>5</sup> he subjected liquid hydrogen to continuous fractionation, and demonstrated the presence of an isotope of mass 2 by optical methods as shown in Plate VIII. This isotope was soon made available in quantities by electrolytic methods of concentration<sup>6</sup> and on account of its unique importance was given the name

<sup>1</sup> *Phys. Rev.*, 43, 103, 1933.

<sup>2</sup> *V.* p. 122.

<sup>3</sup> *Phys. Rev.*, 35, 1015, 1930.

<sup>4</sup> *Ibid.*, 37, 1669, 1931.

<sup>5</sup> *Ibid.*, 39, 164; 40, 1, 1932.

<sup>6</sup> *V.* p. 260.

## I. HYDROGEN

" deuterium " and the symbol D. At the same time the lighter twin was given the name " protium " for use on those comparatively rare occasions when distinction between it and normal hydrogen might be necessary. As has been noted on p. 115 deuterium filled the gap in the natural doublets by which the isotopic weight of  $^1\text{H}$  could be directly ascertained, and when this was done the error, which had had such fortunate results, was clearly revealed.<sup>1</sup> Here we have the pretty paradox of the isotope discovered providing the means to remove that very discrepancy which seemed to point the way so clearly to its discovery.

Following the discovery of deuterium the possibilities of a stable isotope of mass 3 received immediate attention. Direct optical search by Lewis and Spedding<sup>2</sup> gave a negative result. On the other hand mass spectrometer measurements of the effects at mass 5, the  $^2\text{H}^3\text{H}$  molecule, by Lozier, Smith and Bleakney<sup>3</sup> suggested its presence to the extent of 7 parts in  $10^{10}$  of hydrogen. This figure, subsequently withdrawn, was included in the first international table of isotopes in 1936. At the instigation of Lord Rutherford<sup>4</sup> 43·4 kilos of heavy water, resulting from the electrolysis of 13,000 tons of water in Norway, was further electrolysed down to 11 c.c. This was analysed by the writer<sup>5</sup> with his third mass spectrograph, and though a careful search for the hypothetical molecule  $^2\text{H}^3\text{H}$  at mass 5 was made with long exposures no trace of this was found. It was concluded that stable  $^3\text{H}$  cannot exist to anything like the extent of  $10^{-10}$  in ordinary hydrogen. Quite recently Alvarez and Cornog<sup>6</sup> have concluded that the  $^3\text{H}$  produced artificially by the bombardment of deuterium is radioactive.

The first measurement of the isotopic weight of deuterium was made by Bainbridge<sup>7</sup> by means of the  $\text{DH}_2\text{-He}$  doublet shown in Plate VII. The more recent determinations with the latest instruments have been discussed in Chapter X, and it may be concluded that the most reliable values for the isotopic weights of protium and deuterium are those given by Mattauch<sup>8</sup>  $\text{H} = 1.008130 \pm 0.0000033$  and  $\text{D} = 2.014722 \pm 0.0000064$ .

The early estimates of the abundance of deuterium in normal hydrogen, made by optical and mass spectrum methods, were discordant. The figure 0·02 per cent. adopted in the first International Table of Isotopes, and still in use, was founded on protium-deuterium ratios such as  $5000 \pm 500$  for rainwater found by Bleakney and Gould<sup>9</sup>

<sup>1</sup> Aston, *Nature*, **135**, 541, 1935.

<sup>2</sup> *Phys. Rev.*, **43**, 464, 1933.

<sup>3</sup> *Ibid.*, **45**, 655, 1934.

<sup>4</sup> *Nature*, **140**, 303, 1937.

<sup>5</sup> Aston, *Proc. Roy. Soc., A*, **163**, 391, 1937.

<sup>6</sup> *Phys. Rev.*, **56**, 613, 1939.

<sup>7</sup> *Ibid.*, **41**, 115; **42**, 279, 1932.

<sup>8</sup> *Ibid.*, **57**, 1155, 1940.

<sup>9</sup> *Ibid.*, **44**, 265, 1933.

by mass spectrum analysis, and  $5750 \pm 250$  estimated by Johnston<sup>1</sup> by electrolytic methods. Nine values ranging from 5400 to 7020 are considered in the Intl. At. Wt. Report for 1940, and on account of these combined with the isotopic weight of protium the round figure 1.0080 is adopted for the chemical atomic weight.

Confidence in accuracy of measurement and the inviolability of natural constants, which seemed so firmly founded by a century of science, has suffered many shocks in recent years, of which few have been so disturbing as the discovery of heavy hydrogen and its subsequent revelations. Those in respect to the isotopic weight of protium were startling at the time, but the still more recent findings in connection with the atomic weight of hydrogen have a much deeper significance. That the value set by a single observer in a preliminary survey should be out by three or four times his estimated error, even after standing for eight years, was nothing new, but that the accepted figure for an important natural constant, supported by the innumerable and apparently convergent observations of the best chemists and physicists in the world, for over half a century, should be found in error by over ten times its estimated uncertainty was indeed unexpected. Yet the incredible has happened and the familiar figure, founded on Morley's classical work and trusted for so long, has to go into oblivion, to be replaced by an approximate value based exclusively on mass spectrum measurements.

## 2. Helium.

Early in his work with positive rays Sir J. J. Thomson noticed how easy it was to obtain a parabola corresponding to mass 4 both visually and photographically even with the smallest traces of helium present in the discharge tube. In this way he was able to show that the element was liberated from many substances by bombardment with cathode rays.<sup>2</sup> Although the merest trace of helium will record its first-order line on a mass spectrum it was only very much later that its second-order line due to doubly charged helium, the well-known alpha ray of radioactivity, was observed,<sup>3</sup> and used to check the hydrogen-helium ratio of mass.

The possibility of isotopes of mass number 3 and 5 was of great interest, but the result of a search<sup>4</sup> with the first mass spectrograph was completely negative. Later on evidence from transmutation experiments encouraged further efforts to identify these constituents in natural helium, and Tate and Smith<sup>5</sup> from mass spectrum analysis

<sup>1</sup> *J. Amer. Chem. Soc.*, 57, 484, 1935.

<sup>2</sup> J. J. Thomson, *Rays of Positive Electricity*, 2nd ed., 1921.

<sup>3</sup> Aston, *Nature*, 130, 21, 1932.

<sup>4</sup> Aston, *Phil. Mag.*, 45, 935, 1923.

<sup>5</sup> *Phys. Rev.*, 43, 672, 1933.

## 2. HELIUM

of the gas from beryl proved that  ${}^5\text{He}$  was not present to 1 part in 40,000, and Vaughan, Williams and Tate<sup>1</sup> showed the absence of  ${}^3\text{He}$  to the same order. Lord Rutherford<sup>2</sup> reviewing the evidence for  ${}^3\text{He}$  concludes that its absence is probably due to rapid disappearance owing to transmutation. Joliot and Zlotowsky<sup>3</sup> consider that  ${}^5\text{He}$  is certainly stable and though produced in transmutation does not occur in appreciable quantity in natural sources. Quite recently Alvarez and Cornog<sup>4</sup> by using the 100-inch cyclotron as a mass spectrograph, have succeeded in showing that a stable  ${}^3\text{He}$  is present to an abundance of the order of  $10^{-7}$  per cent. It is as well to realize that though logically, therefore, helium is a complex element this is only owing to the fantastic delicacy of the method of detection which, paradoxical as it may sound, also proves experimentally that helium is actually the simplest element in existence.

The first measurements of the packing fraction of helium are of peculiar interest from the fact that the erroneous result obtained had the remarkable consequences, already discussed, in connection with the discovery of deuterium. These measurements were made with the writer's second mass spectrograph<sup>5</sup> and the mass of He compared with that of  $\text{O}^{++}$  by Method III<sup>6</sup> using the known ratio of the lines  $\text{C}^{++}$  and C as a measure. Owing to the insensitive plates then available and the faintness of the second order lines involved, this comparison was extremely difficult and only four measurements were made, which indicated a packing fraction of 5.4 and a mass 4.00216. As this result agreed reasonably well with the data then available from density determinations, there was no reason to doubt its substantial accuracy. It was only eight years later, when the results of transmutations raised doubts as to the validity of so low a mass, and deuterium became available, that the natural doublet  ${}^2\text{D}_2$ - ${}^4\text{He}$  was measured<sup>7</sup> and the error, which had had such fortunate results, was revealed.

Recent determinations of the isotopic weight of  ${}^4\text{He}$  are in good agreement. The writer's second order focusing mass spectrograph gives a packing fraction of 9.77 and a mass  $4.00391 \pm 0.00016$  from measurements of the doublet  ${}^2\text{D}_2$ - ${}^4\text{He}$ .<sup>8</sup> Bainbridge and Jordan, from measurements of the same doublet, give  $4.00395 \pm 0.00007$ ,<sup>9</sup> subsequently reduced to  $4.00389 \pm 0.00007$ .<sup>10</sup> More recently Bain-

<sup>1</sup> *Phys. Rev.*, **46**, 327, 1934.

<sup>2</sup> *Nature*, **140**, 303, 1937.

<sup>3</sup> *Compt. Rend.*, **206**, 17, 1938.

<sup>4</sup> *Phys. Rev.*, **56**, 379, 613, 1939.

<sup>5</sup> Aston, *Proc. Roy. Soc., A*, **115**, 487, 1927.

<sup>6</sup> V. p. 79.

<sup>7</sup> Aston, *Nature*, **135**, 541, 1935.

<sup>8</sup> Aston, *Ibid.*, **137**, 357, 1936.

<sup>9</sup> *Phys. Rev.*, **51**, 385, 1937.

<sup>10</sup> Livingston and Bethe, *Rev. Mod. Phys.*, **9**, 370, 1937.

bridge,<sup>1</sup> from direct comparison with oxygen by means of the doublet  $\text{He}_2\text{-O}$ , gets  $4.00386 \pm 0.00006$ . The present international atomic weight of helium is 4.003 and is based solely on the evidence of mass spectrum analysis.

### 3. *Lithium.*

This metal has received much attention for several reasons. Its mass rays are easy to produce, indeed, it was by the use of its salts that anode rays were discovered, the large relative difference of mass between its isotopes offered unusual possibilities of their separation, and it was the first element shown to be capable of artificial transmutation. Its isotopic constitution was first demonstrated in 1921. The photograph showing the two parabolas of lithium then obtained by the writer from a heated anode<sup>2</sup> is shown in Plate I. Thomson used a composite anode and Dempster, who confirmed the presence of  ${}^6\text{Li}$  shortly afterwards<sup>3</sup> ionized the vapour of the metal itself.

During the early work on transmutation the possibility of a stable isotope of mass 5 was discussed and Brewer<sup>4</sup> reported evidence of a mass 5 present to the extent of 1 part in 20,000. A search by Sampson and Bleakney<sup>5</sup> showed, however, that it was not present to a fifth or probably a tenth of this amount. It seems safe to conclude that terrestrial lithium consists of isotopes 7 and 6 only, and it is an interesting fact that optical work on the solar spectrum has so far provided no evidence of  ${}^6\text{Li}$  in the Sun.

Many experiments have been made to determine the ration of abundance of  ${}^7\text{Li}$  to  ${}^6\text{Li}$ . The first, made by Dempster,<sup>6</sup> gave results indicating ratios so high as 37 and so low as 4.8 with means around 7–10, and are of little value. Morand,<sup>7</sup> using a heated anode and measuring simultaneously the currents carried by  ${}^6\text{Li}$  and  ${}^7\text{Li}$ , arrived at the figure 14.9, a ratio agreeing well with the chemical atomic weight 6.94 on the assumption that the atoms had exact whole-number masses. The reliability of this result is, however, considerably reduced by the fact that Morand's apparatus was not capable of resolving the two atomic streams completely, so that the final figure was only obtained by indirect calculation.

A detailed investigation on the subject was made by Bainbridge<sup>8</sup> who attributed the spurious variation in the ratio observed by Thomson

<sup>1</sup> *Phys. Rev.*, **53**, 922, 1938.

<sup>2</sup> Aston and Thomson, *Nature*, **106**, 828, 1921.

<sup>3</sup> Dempster, *Phys. Rev.*, **18**, 415, 1921.

<sup>4</sup> *Phys. Rev.*, **49**, 635, 1936.

<sup>5</sup> *Ibid.*, **50**, 456, 1936.

<sup>6</sup> Dempster, *Ibid.*, **18**, 415, 1921.

<sup>7</sup> Morand, *Comptes Rendus*, **182**, 460, 1926; *Ann. Physique*, **7**, 164, 1927.

<sup>8</sup> *J. Franklin Inst.*, **212**, 317, 1931.

## 3. LITHIUM

and Dempster to effects of space charge. Bainbridge employed heated spodumene as his source and was able to achieve great constancy with it. He gives three figures, 10.75, 11.28, 11.51, for the ratio of the currents carried by  $^7\text{Li}$  and  $^6\text{Li}$ , concluding that the most probable value is  $11.28 \pm 0.07$ . If we assume that perfect mixing takes place at the source, to get the true relative abundance this figure must be multiplied by the square root of the ratio of the masses so as to correct for the isotope effect in free evaporation<sup>1</sup> giving 12.19. From photometry of the mass spectra obtained from a composite anode the writer roughly estimated the relative intensities of the beams at 11,<sup>2</sup> supporting Bainbridge's value as against the much lower ratio 7.2 calculated from observations on band spectra.<sup>3</sup> Another low value, 8.4, was reported by Harnwell and Bleakney<sup>4</sup> from mass spectrum analysis of rays from heated spodumene, and a similar one of 8.1 from optical data the same year.<sup>5</sup> Brewer has made several investigations on the relative emission of  $^7\text{Li}$  and  $^6\text{Li}$  from heated lithium salts. In his first<sup>6</sup> he got a ratio  $12.14 \pm 0.4$ . Later<sup>7</sup> he found a ratio  $11.60 \pm 0.06$ . This remained practically constant until 40 per cent. of the salt had evaporated, which makes it appear unlikely that ideal conditions for free evaporation are maintained. If the full theoretical correction is applied the ratio of abundance becomes 12.52.<sup>8</sup>

Still more recently Hoff Lu<sup>9</sup> measuring the lithium ion current from heated amblygonite finds the ratio increased rapidly with time in the first hour, became constant for several hours, and then gradually increased again. The ratio of the areas under the time change curves was 12.29. In view of the difficulties of applying a reliable correction the figures of Bainbridge, Brewer and Hoff Lu may be regarded as in good agreement and justifying the value 7.5 for the percentage abundance of  $^6\text{Li}$ . This has been adopted in the International Table for 1940.

The masses of such light nuclei as those of the isotopes of lithium are naturally of the greatest interest in connection with theories of nuclear structure. They were shown to be greater than whole numbers when compared with the carbon line by means of the first mass spectrograph.<sup>10</sup> The first measured values were published by Costa<sup>11</sup> in 1925. He used a composite anode arranged in such a way that

<sup>1</sup> V. p. 254.      <sup>2</sup> Aston, *Proc. Roy. Soc., A*, **134**, 574, 1932.

<sup>3</sup> v. Wijk and v. Koeveringe, *Ibid.*, **A**, **132**, 98, 1931; Nakamura, *Nature*, **128**, 759, 1931.      <sup>4</sup> *Phys. Rev.*, **45**, 117, 1934.

<sup>5</sup> Ornstein, Vreeswyk and Wolfsohn, *Physica*, **1**, 53, 1934.

<sup>6</sup> *Phys. Rev.*, **46**, 894, 1934.      <sup>7</sup> *Ibid.*, **47**, 571, 1935.

<sup>8</sup> Brewer, *J. Chem. Phys.*, **4**, 350, 1935.

<sup>9</sup> *Phys. Rev.*, **53**, 845, 1938.

<sup>10</sup> Aston, *Phil. Mag.*, **47**, 393, 1924.

<sup>11</sup> V. p. 73.

after registering the lithium lines it could be moved away to allow the ordinary gas lines of the discharge to be photographed and compared by the method of bracketing. Assuming the value of He to be exactly 4 he obtained for  ${}^6\text{Li}$  the isotopic weight of 6.009 which the writer's value for He raised to 6.012.<sup>1</sup> In the same way if  ${}^{14}\text{N} = 14.008$  Costa gave for  ${}^7\text{Li}$  7.012. The corresponding packing fractions of 20 and 17 were incorporated in the original packing fraction curve<sup>2</sup> and remained the only ones available for the next six years.

With the epoch making discovery by Cockcroft and Walton<sup>3</sup> in 1932 that lithium disintegrates under bombardment by swift protons and produces alpha particles, the relations between the masses of the nuclei concerned became of great importance, and Bainbridge<sup>4</sup> investigated these by means of his velocity selector instrument.<sup>5</sup> Here he was assisted by the use of the newly discovered heavy hydrogen and succeeded in photographing the natural doublet D<sub>2</sub>- ${}^6\text{Li}$ , a technical achievement of the highest order. With the values of  ${}^1\text{H}$  and  ${}^4\text{He}$  then in use he obtained the isotopic weights 6.0145 and 7.0146. He was then enabled to announce the experimental proof of Einstein's hypothesis of the equivalence of mass and energy. From optical observations of the band spectra given by lithium it is possible to deduce the ratio of the masses of its isotopes. The work of Jenkins and McKellar<sup>6</sup> indicates a ratio differing considerably from the mass spectrum results, on the other hand those of Siga and Plumley<sup>7</sup> and Almy and Irwin<sup>8</sup> are in excellent accord with Bainbridge, and with the virtually identical masses 6.0143 and 7.0148 deduced from observations on disintegration.<sup>9</sup>

When the error in the reference mass of helium was discovered most of the foregoing values became subject to an increase of about 1 in 2000. The only observation on lithium with a modern high resolution instrument is one by Bainbridge and Jordan<sup>10</sup> on the doublet  ${}^7\text{Li}-{}^{14}\text{N}^{++}$  which gives a value  $7.01818 \pm 0.00012$ . No corresponding work has been done with  ${}^6\text{Li}$ . The doublet  ${}^6\text{Li}-{}^{12}\text{C}^{++}$  is clearly ideal for the purpose, but technical difficulties have so far defeated all attempts to produce it. If in Bainbridge's 1933 results we substitute the latest mass of D, the isotopic weight of  ${}^6\text{Li}$  becomes  $6.0177 \pm 0.0003$ . These values are in good agreement with those deduced from more general disintegration data<sup>11</sup> and combine with the abundance ratio

<sup>1</sup> Aston, *Proc. Roy. Soc., A*, **115**, 509, 1927

<sup>2</sup> V. p. 80.

<sup>3</sup> *Proc. Roy. Soc., A*, **136**, 1932.

<sup>4</sup> *Phys. Rev.*, **44**, 56, 1933.

<sup>5</sup> V. p. 83.

<sup>6</sup> *Phys. Rev.*, **44**, 325, 1933; **49**, 205, 1936.

<sup>7</sup> *Ibid.*, **48**, 104, 1935.

<sup>8</sup> *Ibid.*, **49**, 72, 1936.

<sup>9</sup> Oliphant, Kempton and Rutherford, *Proc. Roy. Soc., A*, **149**, 406, 1935.

<sup>10</sup> V. p. 112.

<sup>11</sup> Allison; Smith, *Phys. Rev.*, **55**, 624; **56**, 548, 1939.

## 4. BERYLLIUM

to give an atomic weight on the chemical scale of 6.941 virtually identical with the international one 6.94 derived from chemical data.

#### *4. Beryllium.*

As compared with those of other very light elements the early results with beryllium were unusually scarce and unsatisfactory. That its principal sotope had mass number 9 was shown by means of the parabola method by G. P. Thomson.<sup>1</sup> Later by means of accelerated anode rays applied to the first mass spectrograph this line was found to indicate a slight excess over an integer, but within the accuracy of experiment.<sup>2</sup> In each case rays from an anode containing beryllium fluoride were used, but the effects were feeble in intensity so that other isotopes if present in small quantities could not have been detected.

The possibility of an isotope of mass 8 was of great interest. It was thought that this might disintegrate into two alpha particles<sup>3</sup> and so account for the fact, noted by Lord Rayleigh,<sup>4</sup> that normal beryl contained unexplainably large quantities of helium. Watson and Parker<sup>5</sup> thought that they had detected it in band spectra, but Bleakney,<sup>6</sup> with a mass spectrometer, failed to detect 1 part in 10,000. This work was repeated with the still more sensitive instrument of Nier,<sup>7</sup> who showed that it did not exist to the extent of 1 part in 100,000. Later it was proved that the helium content of beryl is not connected with beryllium at all.<sup>8</sup>

The first precision measurement of the isotopic weight of  ${}^9\text{Be}$  was made by Bainbridge<sup>9</sup> who, comparing it with  ${}^{12}\text{C}$  by means of the ratio C-CH, as shown in Plate VII, obtained a value  $9.0155 \pm 0.0008$ . Later from measurements of the doublets  ${}^{20}\text{Ne}^{++}-{}^9\text{BeH}$  and  ${}^{10}\text{B}-{}^9\text{BeH}$ <sup>10</sup> he found  $9.01517 \pm 0.00016$ . If the writer's value for  ${}^{10}\text{B}$  is substituted in the second doublet we obtain 9.01494 in better accord with the results of disintegration experiments.<sup>11</sup> This corresponds to a packing fraction 16.6, very much higher than that of the other light elements of even atomic number. Correcting to the chemical scale gives an atomic weight of 9.0125, the international one from chemical data is 9.02.

<sup>1</sup> *Phil. Mag.*, **42**, 857, 1921.

<sup>2</sup> Aston, *Ibid.*, **47**, 393, 1924.

<sup>3</sup> Atkinson and Houtermans, *Zeits. Physik.*, **54**, 664, 1929.

<sup>4</sup> *Nature*, **123**, 607, 1929.

<sup>5</sup> *Phys. Rev.*, **37**, 167, 1931.

<sup>6</sup> Bleakney, Blewitt, Stern and Smolochowsky, *Ibid.*, **50**, 545, 1936.

<sup>7</sup> *Ibid.*, **52**, 933, 1937.

<sup>8</sup> Fay, Gluckauf and Paneth, *Proc. Roy. Soc., A*, **165**, 238, 1938.

<sup>9</sup> *Phys. Rev.*, **43**, 367, 1933.

<sup>10</sup> *Ibid.*, **51**, 385, 1937.

<sup>11</sup> Allison, *Ibid.*, **55**, 624, 1939.

*5. Boron.*

The very early discovery of the isotopic nature of boron is due to the fact that it forms a stable gaseous fluoride  $\text{BF}_3$ , which can be introduced into the discharge tube without difficulty. After a failure to obtain a result with boron hydride the fluoride was used mixed with  $\text{CO}_2$ .<sup>1</sup> Very complex and interesting spectra were obtained and it was remarked that the gas possessed an extraordinary power of resurrecting the spectra of gases which had been previously used in the discharge bulb, doubtless due to the chemical action of the fluorine liberated.

After several successful series of spectra had been secured, the percentage of boron trifluoride in the gas admitted was increased as far as possible, until the discharge became quite unmanageable and the tube ceased to work. Just before it did, however, it yielded two very valuable spectra which confirmed the isotopic nature of boron. These are reproduced side by side as they were taken (Spectra I and II, Plate IV). The lines at 10 and 11 are undoubtedly both first-order lines of boron. The hypothesis that these might be due to neon liberated by the action mentioned is not tenable, both on account of their relative intensities and the absence of *strong* neon first-order lines. Even if it were, it could not explain the presence of the well-defined lines at 5 and 5.5 which had never been obtained before at all, and which must be second-order lines of boron. This element therefore has at least two isotopes 10 and 11. The relative photographic intensity of the lines 5 and 5.5 did not agree well with an atomic weight as high as 10.9, the value then in use, and the discrepancy might have been explained by the presence of a third isotope at 12. This would be masked by carbon, for it was not practicable to eliminate carbon from the discharge. But Plate IV, Spectrum IV, contradicts this suggestion, for the line at 49 is mainly if not wholly due to  $^{11}\text{BF}_2$ , so that there should also be a line at 50 for  $^{12}\text{BF}_2$ . The line at 49 is very strong, but at 50 any small effect there may be can safely be ascribed to the fourth order of mercury. The evidence was clearly against the presence of a third isotope and none has been reported since. A revision of the chemical atomic weight removed the apparent discrepancy.

Measurements of the relative abundance of the isotopes of boron are not satisfactory, which is unfortunate, for among complex elements it has the highest known separability,<sup>2</sup> and there is some evidence that its chemical atomic weight may vary with its source.<sup>2</sup>

The photometry of mass spectra derived from boron trifluoride of

<sup>1</sup> Aston, *Phil. Mag.*, **40**, 628, 1920.

<sup>2</sup> V. p. 211.

unascertained but probably European origin<sup>1</sup> gave a ratio of abundance of isotope 11 to isotope 10 of 3·85, not of high accuracy owing to the large correction for the position of the lines. This ratio must necessarily be too low as the photograph effect of the lighter isotope must certainly be enhanced by its greater velocity and penetrating power. The correction is not ascertainable, but if we make the rough assumption that it is proportional to the velocity the ratio will be 4·04. The ratio of the abundance of the boron isotopes has also been measured by means of band spectra. Elliott<sup>2</sup> from photometry of the bands of BO (Chilian boron) estimates it to be  $3\cdot63 \pm 0\cdot02$ . On the other hand, from observations on the bands of BH Paton and Almy<sup>3</sup> give the much higher figure  $4\cdot86 \pm 0\cdot15$ .

The relative heights of the peaks of ionisation current in the separation experiments of Yates<sup>4</sup> suggest a ratio rather greater than 4, but owing to the conditions of the experiment are not strictly valid for abundance. In the international table the round figures 20 and 80 have been adopted for the percentage abundances of  $^{10}\text{B}$  and  $^{11}\text{B}$  respectively.

The packing fractions of both isotopes of boron were measured in the writer's first survey.<sup>5</sup> As before boron trifluoride was used to give the lines of the element. The lighter isotope  $^{10}\text{B}$  was compared with O<sup>++</sup> by the use of the known ratio CH<sub>3</sub> : C.  $^{11}\text{B}$  was compared with C by the ratio C : CH which is sufficiently near for the purpose. The results so obtained were checked by comparing the ratio  $^{10}\text{B} : ^{11}\text{B}$  with that of  $^{11}\text{B} : \text{C}$ . The packing fraction of  $^{10}\text{B}$  was estimated at 13·5 and that of  $^{11}\text{B}$  at 10·0.

When instruments of higher resolving power became available much more accurate determinations were made. From the natural doublet  $^{20}\text{Ne}^{++-10}\text{B}$  the writer deduced a packing fraction for  $^{10}\text{B}$ , of 16·1 and an isotopic weight  $10\cdot0161 \pm 0\cdot0003$ .<sup>6</sup> From the same doublet and also from doublet  $^{10}\text{BH}_2-^{12}\text{C}$  Bainbridge<sup>7</sup> gets a higher value  $10\cdot01633 \pm 0\cdot00013$ . From doublets  $^{10}\text{BH}-^{11}\text{B}$  and  $^{11}\text{BH}-^{12}\text{C}$  he also obtains a value for  $^{11}\text{B}$  of  $11\cdot01295 \pm 0\cdot00013$ . Disintegration data in general suggest rather lower masses for the isotopes of boron.<sup>8</sup> Using the data provided by mass spectra and correcting to the chemical scale the atomic weight of boron works out at 10·81. The accepted value from chemical observations is 10·82.

<sup>1</sup> Aston, *Proc. Roy. Soc., A*, **132**, 490, 1931.

<sup>2</sup> Elliott, *Nature*, **126**, 845, 1930.

<sup>3</sup> Paton and Almy, *Phys. Rev.*, **37**, 1710, 1931.

<sup>4</sup> *Proc. Roy. Soc., A*, **168**, 148, 1938.

<sup>5</sup> Aston, *Ibid.*, **A**, **115**, 502, 1927. <sup>6</sup> *Nature*, **137**, 613, 1936.

<sup>7</sup> *Phys. Rev.*, **51**, 385, 1937. <sup>8</sup> Allison, *Ibid.*, **55**, 624, 1939.

***6. Carbon.***

The importance of this element in the development of mass ray analysis can hardly be overestimated. It is invariably present in the ordinary discharge and its lines and those of its compounds were from the first used as reference lines. There was no positive indication whatever to suppose it to be otherwise than simple and of mass number 12,<sup>1</sup> and the very close integral relation between its chemical atomic weight and that of oxygen strongly supported this conclusion. Carbon and its hydrides form well-marked groups of reference lines which were of the greatest value in developing the scale of mass. The first, which may be called the C<sub>1</sub> group, contains five lines, 12—C, 13—CH, 14—CH<sub>2</sub>, 15—CH<sub>3</sub>, 16—CH<sub>4</sub> and is well shown in Spectrum V, Plate III, and also under greater power of resolution in Spectrum I, Plate VI. The second or C<sub>2</sub> group 24—C<sub>2</sub>, 25—C<sub>2</sub>H—also appears frequently, derived from hydrocarbons in the wax and grease used in the joints of the apparatus. It can be seen in Spectra I, II, III, Plate III. The higher groups C<sub>3</sub> and C<sub>4</sub> appear, for some obscure reason, when metallic methyls and carbonyls are present.

The discovery of the isotopes of oxygen introduced a discrepancy in atomic weights which suggested the existence of a higher isotope of carbon and in 1929 King and Birge<sup>2</sup> from observations on the band spectra of C<sub>2</sub> were able to announce the discovery of a rare isotope <sup>13</sup>C. The presence of this was later confirmed by Birge<sup>3</sup> in the band spectra of CO and CN. In their later report<sup>4</sup> from which the illustration, Plate VIII, is taken King and Birge conclude that the masses of the two isotopes of carbon are integrally related to 1 part in 10,000 and estimate the ratio of abundance as 400. The latter is admittedly uncertain as the strength of the isotopic band relative to the primary one may depend upon the excitation conditions. Thus they found that it appeared many times less abundant in the arc than in the furnace. In addition it has been observed<sup>5</sup> that in some R and N types of stars the <sup>12</sup>C<sup>13</sup>C band is quite abnormally intense, though it seems highly improbable that the ratio should be altogether different to that found in terrestrial carbon.

The abundance of <sup>13</sup>C was first estimated by photometry of mass spectra by means of its second order line at 6·5, a faint line which had been actually observed very early in the work, and noted as "a line of unknown origin."<sup>6</sup> This was compared with the strong line at 6

<sup>1</sup> Aston, *Phil. Mag.*, **39**, 619, 1920.

<sup>2</sup> *Phys. Rev.*, **30**, 825, 1929.

<sup>3</sup> *Nature*, **124**, 13, 1929.

<sup>4</sup> *Astrophys. J.*, **72**, 251, 1930.

<sup>5</sup> Sanford, *Pub. Ast. Soc. Pacific*, **41**, 271, 1929.

<sup>6</sup> Aston, *Phil. Mag.*, **40**, 632, 1920.

## 7. NITROGEN

and the ratio estimated as  $140 \pm 14$ .<sup>1</sup> A lower figure  $91.6 \pm 2.2$  was obtained with the mass spectrometer of Vaughan, Williams and Tate,<sup>2</sup> which was subsequently supported by the work of Brosi and Harkins<sup>3</sup> on band spectra who gave  $92.2 \pm 3.7$ . A very thorough investigation of the problem has been quite recently made by Nier and Gulbransen,<sup>4</sup> who show that the ratio varies with the origin of the carbon, and give as their mean  $90 \pm 2$ . This corresponds to percentages 98.9 and 1.1 for  $^{12}\text{C}$  and  $^{13}\text{C}$  respectively which have been adopted in the table.

The packing fraction of  $^{12}\text{C}$  is of great importance on account of its use as a substandard of mass. It was first measured by the use of artificial doublets using the approximate geometrical progression  $\text{O} : \text{C} : \text{OH}_2$  and the value 3.0 obtained was checked by means of the natural doublet  $\text{CH}_4-\text{O}$ .<sup>5</sup> This corresponds to an isotopic weight 12.0036. After the discovery of deuterium the development of mass spectrographs of higher power enabled the masses of  $^1\text{H}$ ,  $^{12}\text{C}$  and  $^{16}\text{O}$  to be correlated by natural doublets.<sup>6</sup> In this way the writer obtained the value  $12.0035 \pm 0.0003$ <sup>7</sup> and Bainbridge and Jordan<sup>8</sup> the higher value  $12.00428 \pm 0.00017$ . Later the writer<sup>9</sup> using a number of different methods deduced a packing fraction of 2.96 and mass  $12.00355 \pm 0.00015$  and Bainbridge's value was reduced to  $12.00398 \pm 0.00009$ .<sup>10</sup> More recently Mattauch<sup>11</sup> obtained  $12.003876 \pm 0.000032$ , and his latest value<sup>12</sup>  $12.003861 \pm 0.000024$  is probably the most reliable yet given.

The isotopic weight of  $^{13}\text{C}$  can be deduced from Bainbridge and Jordan's<sup>13</sup> measurement of the doublet  $^{12}\text{CH}-^{13}\text{C}$  tabulated on p. 112. Using the latest figures for the substandards this gives  $13.00749 \pm 0.00015$ . On the other hand Jenkins and Woolridge<sup>14</sup> by observation of band spectra deduce a higher figure 13.0088. If Nier's estimate for the relative abundance of the isotopes is used the atomic weight of carbon is 12.011 in excellent accord with the international chemical value 12.010.

## 7. Nitrogen.

Owing to its presence in the air this element was one of the first recorded by positive ray analysis. Its examination by the first mass spectrograph was difficult, as its atom could not be distinguished from

<sup>1</sup> Aston, *Nature*, **134**, 178, 1934.      <sup>2</sup> *Phys. Rev.*, **46**, 327, 1934.

<sup>3</sup> *Ibid.*, **52**, 472, 1937.      <sup>4</sup> *J. Amer. Chem. Soc.*, **61**, 697, 1939.

<sup>5</sup> Aston, *Proc. Roy. Soc., A*, **115**, 487, 1927.      <sup>6</sup> V. p. 115.

<sup>7</sup> Aston, *Nature*, **137**, 357, 1936.

<sup>8</sup> *Phys. Rev.*, **51**, 385, 1937.      <sup>9</sup> Aston, *Nature*, **139**, 922, 1937.

<sup>10</sup> *Rev. Mod. Phys.*, **9**, 368, 1937.      <sup>11</sup> *Zeit. tech. Phys.*, **12**, 578, 1938.

<sup>12</sup> *Phys. Rev.*, **57**, 1155, 1940.      <sup>13</sup> *Ibid.*, **49**, 883, 1936.

<sup>14</sup> *Ibid.*, **49**, 882, 1936; **53**, 137, 1938.

$\text{CH}_2$ , nor its molecule from  $\text{CO}$ . Its second-order line appeared to correspond to a mass exactly 7,<sup>1</sup> and it was assumed to be a simple element, as was to be expected from its chemical atomic weight 14.008.

The determination of its packing fraction by means of the second mass spectrograph<sup>2</sup> was unsatisfactory owing to the impossibility of disentangling its lines from those of carbon compounds, while at the same time making use of the latter for reference ratios. By the use of mixtures of nitrogen and ethane in varying proportions some success was obtained, and the results indicated the most probable value of its packing fraction to be 6.0 giving a mass 14.008.

The discovery of the isotopic nature of oxygen and the resulting shift of the mass scale led to a search for heavier isotopes of nitrogen and the second rare component 15 was discovered by Naudé<sup>3</sup> in the band spectra of  $\text{NO}$ . In his later report<sup>4</sup> he estimates the ratio of abundance of  $\text{N}^{14}$  to  $\text{N}^{15}$  to be  $700 \pm 140$ . Naudé's work was supported by that of Herzberg<sup>5</sup> who estimated the ratio at 800. Herzberg also searched for an isotope 16, theoretically predicted, but this was not found. Later estimates of the ratio of abundance are considerably lower. Birge and Menzel<sup>6</sup> taking Mecke's values for the oxygen isotopes, calculate that it should be 320 in order to bring the writer's figure for the mass of  $^{14}\text{N}$  into agreement with the chemical atomic weight. Urey and Murphy<sup>7</sup> from their measurement of absorption bands give for the ratio of abundance of  $^{15}\text{N}^{16}\text{O}$  to  $^{14}\text{N}^{18}\text{O}$  the preliminary value  $0.551 \pm 0.062$ . Assuming Mecke's value for the ratio  $^{16}\text{O}$  to  $^{18}\text{O}$  this gives for the nitrogen ratio 347. Later direct measurements of the ratio by means of a mass spectrometer by Vaughan Williams and Tate<sup>8</sup> gave  $265 \pm 8$ , a figure which was confirmed by Wahl, Hoffman and Hipple,<sup>9</sup> and has been adopted in the table in the form of the percentages 99.62 and 0.38.

The isotopic weight of  $^{14}\text{N}$  can be conveniently compared with substandards by the natural doublet  $^{12}\text{CH}_2$ — $^{14}\text{N}$ . The difference in mass was first measured by the writer with his third mass spectrograph as 0.01274.<sup>10</sup> Later values are Bainbridge and Jordan 0.01274<sup>11</sup> Mattauch 0.012581,<sup>12</sup> Asada, Okuda, Ogata and Yoshimoto 0.01257,<sup>13</sup> and quite recently Jordan, with his latest high dispersion instrument,

<sup>1</sup> Aston, *Phil. Mag.*, **39**, 621, 1920.

<sup>2</sup> Aston, *Proc. Roy. Soc., A*, **115**, 503, 1927.

<sup>3</sup> Naudé, *Phys. Rev.*, **34**, 1498, 1929. <sup>4</sup> *Ibid.*, **36**, 333, 1930.

<sup>5</sup> Herzberg, *Zeit. Phys. Chem.*, Bd. **9**, 43, 1930.

<sup>6</sup> Birge and Menzel, *Phys. Rev.*, **37**, 1669, 1931.

<sup>7</sup> Urey and Murphy, *Ibid.*, **38**, 575, 1931.

<sup>8</sup> *Ibid.*, **46**, 327, 1934.

<sup>9</sup> *J. Chem. Phys.*, **3**, 434, 1935.

<sup>10</sup> Aston, *Nature*, **137**, 613, 1936.

<sup>11</sup> *Rev. Mod. Phys.*, **9**, 370, 1937.

<sup>12</sup> *Zeit. tech. Phys.*, **12**, 581, 1938.

<sup>13</sup> *Nature*, **143**, 797, 1939.

## 8. OXYGEN

gives 0.01256.<sup>1</sup> The last figure if combined with Mattauch's values for C and H<sup>2</sup> gives for the isotopic weight of <sup>14</sup>N the value 14.00756.

Bainbridge and Jordan (*ibid.*) also measured the doublet <sup>14</sup>NH-<sup>15</sup>N and their determination when combined with the value of <sup>14</sup>N given above gives an isotopic weight for <sup>15</sup>N of 15.00495. These isotopic weights used with the abundance ratio give an atomic weight 14.0075 virtually identical with the international chemical one 14.008.

## 8. Oxygen.

This element, the most abundant in Nature and the primary standard of chemical atomic weights, is present, in chemical combination, in all ordinary forms of discharge tube and so may be expected to appear to a greater or less extent on all mass spectra obtained by their means. During the early work on positive ray analysis its molecular line at 32 and its atomic lines of the first and second order at 16 and 8 were, very naturally, chosen as convenient standards of mass. When by means of the second mass spectograph accuracies of the order of 1 in 10,000 were attained and the deviations from the whole-number rule measured, oxygen was defined to have a zero packing fraction and its neutral atom <sup>16</sup>O definitely adopted as the standard of atomic mass on the physical scale. The results then obtained<sup>3</sup> appeared in good accordance with the generally accepted idea that oxygen was essentially a simple element and that therefore the chemical and physical scales were virtually identical ; the disintegration photographs of Blackett<sup>4</sup> suggested that <sup>17</sup>O was at least capable of existence, but no evidence of its presence in appreciable quantity had been observed.

Much interest was raised in 1929 by the announcement by Giauque and Johnston<sup>5</sup> of an isotope of mass 18. Direct measurements with the mass spectrograph showed that it could not be present to an extent greater than in 500,<sup>6</sup> and a later communication from the discoverers<sup>7</sup> gave an estimate of abundance well below that estimate and also announced a further discovery of a still rarer isotope 17. These discoveries were made by the analysis of the spectra of the atmospheric absorption bands photographed by Dieke and Babcock,<sup>8</sup> which when interpreted on the quantum theory afforded unambiguous proof of the existence of molecules <sup>16</sup>O<sup>18</sup>O and <sup>16</sup>O<sup>17</sup>O in the atmosphere.

The determination of the relative abundance is a matter of some

<sup>1</sup> *Phys. Rev.*, **58**, 1009, 1940.

<sup>2</sup> *V. p.* 116.

<sup>3</sup> Aston, *Proc. Roy. Soc., A*, **115**, 487, 1927.

<sup>4</sup> Blackett, *Ibid.*, **A**, **107**, 349, 1925.

<sup>5</sup> Giauque and Johnston, *Nature*, **123**, 318, 1929.

<sup>6</sup> Aston, *Ibid.*, **123**, 488, 1929.

<sup>7</sup> Giauque and Johnston, *Ibid.*, **123**, 831, 1929.

<sup>8</sup> Dieke and Babcock, *Proc. Nat. Acad. Sci.*, **13**, 670, 1927.

difficulty. The first estimate of the ratio  $^{16}\text{O}$  to  $^{18}\text{O}$  was given by Babcock<sup>1</sup> as 1250 with a probable error of 25 per cent. Naudé,<sup>2</sup> working with the absorption bands of NO, which present certain advantages over those of oxygen, gave a value  $1075 \pm 110$ . Later from an exhaustive examination of the atmospheric absorption bands Mecke and Childs<sup>3</sup> give as their best mean 630. They give for the ratio of  $^{18}\text{O}$  to  $^{17}\text{O}$  a value 5 as against 8 estimated by Babcock and Naudé.

Smythe and Mattauch<sup>4</sup> investigated the intensity of the peaks of lines 32 and 34 given by a discharge in oxygen by means of their mass spectrometer and concluded that the ratio of  $^{16}\text{O}$  to  $^{18}\text{O}$  is greater than 600. The intensities of the molecular lines of oxygen have been compared directly by the second mass spectrograph, their brightness being enhanced by the presence of helium in the discharge.<sup>5</sup> Line 32 was found to be 268 times as intense as line 34, which was 4·2 times as intense as line 33. These figures correspond to ratios of abundance 536 and 4·2. Smythe<sup>6</sup> on reinvestigation using samples carefully prepared from  $\text{PbO}_2$  obtained the value  $503 \pm 10$  for the  $^{16}\text{O} : ^{18}\text{O}$  ratio, and Bleakney and Hipple<sup>7</sup> by the mass spectrometer analysis of over 100 samples from a variety of sources, some meteoric, obtained ratios all ranging closely round 500. Further confirmation has recently been obtained by Murphrey<sup>8</sup> using Nier's precision mass spectrometer. He gives for the  $^{16}\text{O} : ^{18}\text{O}$  ratio  $500 \pm 15$  and the  $^{18}\text{O} : ^{17}\text{O}$  ratio  $4\cdot9 \pm 0\cdot2$ . The international figures for abundance now adopted are:

Mass number	16	17	18
Abundance	99.76	0.04	0.20

and the ratio of the chemical to the physical scale of weight now generally accepted is 1.000275.

The isotopic weight of  $^{18}\text{O}$  was first computed at 18.0065 by Babcock and Birge<sup>9</sup> from observations on the vibrational isotope effect in band spectra. Mattauch, from measurements of the doublet  $^{16}\text{OH}_2 - ^{18}\text{O}$ <sup>10</sup> obtained a much lower value  $18.0037 \pm 0.0007$ . On the other hand measurements of the same doublet by the writer<sup>11</sup> gave  $18.0057 \pm 0.0002$  in better agreement with the optical value and corresponding to a packing fraction 3·2. No mass spectrum data on the isotopic weight of the very rare isotope  $^{17}\text{O}$  are yet available, but the disintegration results of Burcham and Smith<sup>12</sup> indicate a value 17.0045.

<sup>1</sup> Babcock, *Ibid.*, **15**, 471, 1929; *Phys. Rev.*, **34**, 540, 1929.

<sup>2</sup> Naudé, *Phys. Rev.*, **34**, 333, 1930.

<sup>3</sup> Mecke and Childs, *Zeit. Physik.*, **68**, 362, 1931.

<sup>4</sup> Smythe and Mattauch, *Phys. Rev.*, **40**, 429, 1932.

<sup>5</sup> Aston, *Nature*, **130**, 22, 1932.

<sup>6</sup> *Phys. Rev.*, **45**, 299, 1934.

<sup>7</sup> *Ibid.*, **47**, 800, 1935.

<sup>8</sup> *Ibid.*, **59**, 320, 1941.

<sup>9</sup> *Ibid.*, **37**, 233, 1931.

<sup>10</sup> *Ibid.*, **50**, 617, 1936.

<sup>11</sup> Aston, *Nature*, **139**, 922, 1937.

<sup>12</sup> *Proc. Roy. Soc., A*, **168**, 176, 1938.

### 9. Fluorine.

So far the most convenient source of fluorine rays is the gas boron fluoride. When this compound was first examined<sup>1</sup> a strong line at 19 with a second order line at 9·5 led to the conclusion that these were due to fluorine which, on account of its chemical atomic weight, was assumed to be simple. The line 20 which appeared in some spectra was clearly due to HF. Spectra given by  $\text{BF}_3$  are reproduced in Plate IV.

The packing fraction of fluorine was measured on the second mass spectrograph<sup>2</sup> by means of the approximate ratio  $\text{C} : \text{CH}_3, \text{F} : \text{C}_2$ . Spectra III and IV, Plate V, are examples of the results; the measurements gave negligibly small packing fractions as often negative as positive, with a mean practically zero.

A more accurate figure has been more recently obtained by the measurement of the natural doublet  $\text{HDO}-\text{F}$ <sup>3</sup> which, when corrected to the latest values of H and D gives a packing fraction 2·36 and an isotopic weight  $19\cdot0045 \pm 0\cdot0006$ . Changing to the chemical scale this corresponds to an atomic weight practically identical with the international one 19·00.

### 10. Neon.

A full account of the early work on neon has already been given in Chapter IV. A faint line at 21 was noticed in the mass spectra then obtained which suggested a third isotope. When it was realized that such an effect might be caused by an abnormal hydride it was considered safer to drop the figure from the tables until more definite evidence of its cause was available. In 1928 Hogness and Kvalnes<sup>4</sup> working under conditions unfavourable to the formation of a hydride obtained conclusive evidence of the occurrence of  $^{21}\text{Ne}$ .

Apart from rough estimates the first measurements of the relative abundance of the three isotopes of neon were made by Bleakney,<sup>5</sup> who also proved the absence of other isotopes to a high degree. For first order lines he found 100 : 0·28 : 8·2 and for second order lines 100 : 0·30 : 9·2 for the mass numbers 20, 21, 22 respectively. Later work by Vaughan, Williams and Tate<sup>6</sup> gave as the ratio  $20 : 21 = 337 \pm 20$  and  $20 : 22 = 9\cdot25 \pm 0\cdot08$ . These figures were adopted in the table giving for the percentage composition of neon :

Mass number	.	.	.	.	20	21	22
Abundance	.	.	.	.	90·00	0·27	0·73

<sup>1</sup> Aston, *Phil. Mag.*, **40**, 629, 1920.

<sup>2</sup> Aston, *Proc. Roy. Soc., A*, **115**, 487, 1927.

<sup>3</sup> Aston, *Nature*, **137**, 613, 1936.

<sup>4</sup> Hogness and Kvalnes, *Phys. Rev.*, **32**, 942, 1928.

*bid.*, **43**, 1056, 1933.

<sup>6</sup> *Ibid.*, **46**, 327, 1934.

The first estimates of the packing fractions of the two principal isotopes of neon were made by the writer with his second mass spectrograph.<sup>1</sup>  $^{20}\text{Ne}$  was compared with O by means of the ratio  $\text{CH}_3 : \text{C}$  and a practically negligible packing fraction was suggested.  $^{22}\text{Ne}$  was then compared with  $^{20}\text{Ne}$  by means of the ratio  $\text{CH} : \text{C}$  and a rough provisional value 2.2 obtained. Seven years later Bainbridge<sup>2</sup> measured the masses by an entirely different method, using his velocity selector instrument.<sup>3</sup> As a mean of ten different measurements of the line  $^{20}\text{Ne}$  against lines of known mass he gave the value  $19.99671 \pm 0.0009$  which corresponds to a packing fraction of  $-0.16$ . By comparing doubly charged  $^{22}\text{Ne}$  with other lines he deduced a value  $21.99473 \pm 0.00087$  and a packing fraction  $-0.24$ . In 1936 the natural doublet  $\text{D}_2\text{O}-^{20}\text{Ne}$  was measured with the writer's third mass spectrograph.<sup>4</sup> This indicated a packing fraction of  $-0.70$  and an isotopic weight of  $19.9986 \pm 0.0006$ . Bainbridge and Jordan<sup>5</sup> from the same doublet got  $19.99917 \pm 0.00019$ , which was later reduced<sup>6</sup> to  $19.99881 \pm 0.00011$ . Mattauch's latest value deduced from doublet  $\text{CD}_4-^{20}\text{Ne}$ <sup>7</sup> is  $19.99896 \pm 0.000066$ .

The only recent data on the rarer isotopes of neon are provided by Bainbridge and Jordan who measured the doublets  $^{20}\text{NeH}-^{21}\text{Ne}$ ,  $^{10}\text{BH}-^{22}\text{Ne}^{++}$  and  $^{11}\text{B}-^{22}\text{Ne}^{++}$ <sup>8</sup> from which were later deduced<sup>9</sup> the isotopic weights  $20.99968 \pm 0.00023$  and  $21.99864 \pm 0.00036$  for  $^{21}\text{Ne}$  and  $^{22}\text{Ne}$  respectively.

With the percentage abundance given above the atomic weight works out at 20.190, virtually identical with the international chemical one 20.183, deduced from density observations.

### 11. Sodium.

Like those of lithium the anode rays of sodium are easy to obtain. Its parabola is indicated in the picture of the lithium parabolas in Plate I. When examined with the first mass spectrograph it gave one line only<sup>10</sup> and was assumed to be simple of mass number 23. The analysis made by Bainbridge<sup>11</sup> supported this conclusion. Using rays from heated jadeite he was able to prove that mass numbers 21 and 25 could not be present to the extent of 1 in 3000, nor 22 to the extent of 1 in 800. More recently Brewer<sup>12</sup> obtained evidence of a

<sup>1</sup> Aston, *Proc. Roy. Soc., A*, **115**, 487, 1927.

<sup>2</sup> *Phys. Rev.*, **43**, 424, 1933.

<sup>3</sup> V. p. 84.

<sup>4</sup> Aston, *Nature*, **137**, 613, 1936.

<sup>5</sup> *Phys. Rev.*, **51**, 385, 1937.

<sup>6</sup> *Rev. Mod. Phys.*, **9**, 370, 1937.

<sup>7</sup> *Zeit. tech. Phys.*, **12**, 578, 1938.

<sup>8</sup> *Phys. Rev.*, **51**, 385, 1937.

<sup>9</sup> *Rev. Mod. Phys.*, **9**, 370, 1937.

<sup>10</sup> Aston, *Phil. Mag.*, **42**, 436, 1921.

<sup>11</sup> Bainbridge, *J. Franklin Inst.*, **212**, 317, 1931.

<sup>12</sup> *Phys. Rev.*, **49**, 856, 1936.

peak at mass number 22 which suggested the presence of  $^{22}\text{Na}$  to about 1 in 5000. On the other hand Sampson and Bleakney<sup>1</sup> failed to find any trace of  $^{22}\text{Na}$  even to 1 in 50,000. From work on transmutation it appears probable that  $^{22}\text{Na}$  is not stable.<sup>2</sup>

No definite value for the packing fraction of  $^{23}\text{Na}$  is yet available from mass spectrum work. Dempster<sup>3</sup> photographed its first order line between the second order lines of  $^{68}\text{Zn}$  and  $^{70}\text{Zn}$  and gives the difference in packing fraction as  $4.9 \pm 0.5$ . From general data of disintegration Pollard<sup>4</sup> deduces an isotopic weight 22.99680. This corresponds to a chemical atomic weight 22.990 very slightly lower than the international one 22.997.

### 12. Magnesium.

Magnesium was the first metal to be analysed by means of its anode rays. Dempster announced the discovery of its three isotopes in December, 1920.<sup>5</sup>

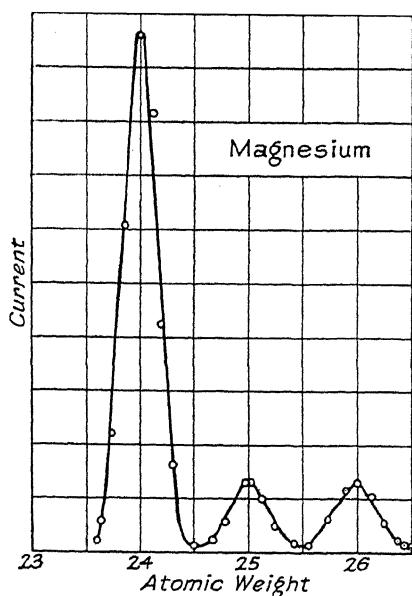


FIG. 35.—Curve for Magnesium.

Its mass rays were obtained with anodes of two types. In the first experiments the heating coil was wound directly on a rod of magnesium, and the whole covered with a glass tube having a hole 3 mm. in diameter between the magnesium and the cathode to restrict the electron bombardment. Later an anode of the type illustrated in Fig. 17 was used. With both types three components with atomic weights 24, 25 and 26 were found. They appeared together as the magnesium was heated so as to vaporize slightly, and their atomic weights could be checked by comparison with rays at 28, probably due to occluded nitrogen, which is driven off before the rays of the metal appear. The relative proportions of the isotopes as indicated by the heights of their peaks on the curves obtained varied somewhat in the earlier experiments. The curve given in Fig. 35 was made from observations with the later

<sup>1</sup> *Phys. Rev.*, 50, 456, 1836.

<sup>2</sup> Laslett, *Ibid.*, 50, 388, 1936.

<sup>4</sup> *Ibid.*, 57, 1186, 1940.

<sup>3</sup> *Ibid.*, 53, 64, 1938.

<sup>5</sup> Dempster, *Science*, Dec. 10, 1920.

type of anode.<sup>1</sup> It is drawn with the maximum of the lighter component exactly at 24, although its position was not compared in this case with the gas line at 28 to the accuracy indicated in the curve. The component at 24 is about 6.7 times as strong as the one at 25, while the latter is about 1.04 times as strong as the one at 26. These correspond to the following composition :

Mass number	24	25	26
Abundance	77.4	11.5	11.1

giving a mean mass number 24.336. The chemical atomic weight of magnesium is 24.32.

As Dempster's observations did not afford an accurate measurement of the masses of the isotopes, except relative to each other, the element was later investigated with the first mass spectrograph by the method of accelerated anode rays.<sup>2</sup> An anode mixture containing the chloride was used and with some difficulty the line 24 was obtained and measured against  $^{23}\text{Na}$ . It showed no deviation from an integer. The effects were too feeble for the other lines to be seen. The lines of magnesium have not yet been examined with an instrument of high precision so no data are available on its packing fraction, the isotopic weights of its components can however be inferred from disintegration data and the latest values given by Pollard<sup>3</sup> are 23.99189, 24.99277 and 25.99062 respectively.

### 13. Aluminium.

From the close approximation of its chemical atomic weight to an integer and the rule concerning the isotopes of elements of odd atomic number aluminium was from the first expected to be simple.<sup>4</sup> During some experiments on tellurium chloride with the first mass spectrograph the chlorine liberated attacked the electrodes unmistakably. In fact, the slit in use was ruined by the corrosion. It is therefore perfectly certain that volatile aluminium chloride must have been present in quantity during the exposures. The indication of its presence was equally strong on the mass spectra obtained. The line at 27, usually very much weaker than that at 28, was very intense, and its second order line easily visible at 13.5. Furthermore, strong groups of lines appeared with their first units at 62 and 97. The intensities of the lines in these groups show that they are due to the mono- and dichlorides of bodies having masses 27 and 28. The latter may be an atom of  $^{28}\text{Si}$  or a molecule of CO, but the only possible origin of the former is an atom of aluminium.

<sup>1</sup> Dempster, *Phys. Rev.*, **18**, 421, 1921.

<sup>2</sup> Aston, *Phil. Mag.*, **47**, 393, 1924.

<sup>3</sup> *Phys. Rev.*, **57**, 1186, 1940.

<sup>4</sup> Aston, *Phil. Mag.*, **40**, 633, 1920.

When a further attack on tellurium chloride was made with the second mass spectrograph<sup>1</sup> a strong line at 27 was obtained on a plate showing no trace of the C<sub>2</sub> group. It was therefore reasonably certain that the element consists mainly of atoms of mass number 27. No evidence of any other stable isotope has so far been given. The packing fraction of aluminium could not be measured until the increased resolving power of the writer's third instrument enabled the doublet C<sub>2</sub>H<sub>3</sub>—<sup>27</sup>Al to be tackled.<sup>2</sup> This yielded for the mass difference a provisional value 0.0405. Putting in Mattauch's values for C and H the isotopic weight of <sup>27</sup>Al becomes 26.9916 and its packing fraction — 3.1. Correcting for difference of scale this gives a chemical atomic weight of 26.984 as compared with the international value 26.97.

#### 14. Silicon.

It is obvious that there is always a possibility of this element appearing in rays from ordinary discharge bulbs on account of its occurrence in the glass walls. The presence of its principal isotopes 28 and 29 was first demonstrated in spectra taken with BF<sub>3</sub><sup>3</sup> and reproduced in Plate IV. The reasoning was as follows :

Consider first the group of three very strong lines 47, 48, and 49. The last two are to be expected as being due to <sup>10</sup>BF<sub>2</sub> and <sup>11</sup>BF<sub>2</sub>, respectively, but since there is no evidence of a boron 9 or a fluorine 18, line 47 cannot be due to a compound of these elements. But line 47 only appeared when BF<sub>3</sub> was introduced, and so must be due to silicon fluoride formed by the action of the fluorine on the glass walls and the silica anticathode.

To test this the BF<sub>3</sub> was washed out and replaced by SiF<sub>4</sub>, which had been made by the action of sulphuric acid on calcium fluoride and silica in the usual way. This greatly reduced the lines 48 and 49, and so they must be attributed to boron compounds. At the same time line 47 remained very strong, and was evidently due to a compound <sup>28</sup>SiF, so that silicon has a predominant constituent 28. This conclusion is further supported by the presence of very strong lines at 66, <sup>28</sup>SiF<sub>2</sub> and 85, <sup>28</sup>SiF<sub>3</sub>.

The chemical atomic weight then accepted as 28.3 indicated that this could not be its only constituent. Lines at 29, 48, 67, and 86 all suggest a silicon of atomic weight 29. Practically conclusive proof of this is given in Spectrum V, Plate IV, which shows its second order line unmistakably at 14.50. The only other reasonable origin of this line, namely second order <sup>10</sup>BF, is eliminated by the fact that there is no trace of a line at 10 in this spectrum.

<sup>1</sup> Aston, *Proc. Roy. Soc., A*, **132**, 494, 1931.

<sup>2</sup> Aston, *Nature*, **137**, 613, 1936.

<sup>3</sup> Aston, *Phil. Mag.*, **40**, 628, 1920.

The presence of a silicon of mass number 30 was suggested by the lines 30, 49, 68, 87, but the possibilities of hydrogen compounds made this inconclusive. Valuable confirmation of this isotope was afforded later by the analysis of the band spectra of silicon nitride by Mulliken,<sup>1</sup> and conclusive proof was afforded by mass spectra obtained during the work on zirconium,<sup>2</sup> when all three lines of silicon were obtained under circumstances which precluded the presence of hydrides.

Partly no doubt owing to the difficulty of obtaining its lines uncontaminated there are no mass spectrum measurements of the relative abundance of the isotopes of silicon yet available. The work of McKellar<sup>3</sup> on photometry of the bands of SiN indicated the following percentages :

Mass number	28	29	30
Abundance	89.6	6.2	4.2

which have been adopted in the table.

During some work with the second mass spectrograph on  $\text{BF}_3$ ,<sup>4</sup> on some of the spectra a faint line could be seen corresponding to a mass of  $9\frac{1}{2}$  which was clearly due to  $^{28}\text{Si}^{+++}$  and provided an opportunity of obtaining a provisional value of its packing fraction. This line was compared with that of  $^{19}\text{F}^{++}$  which was then thought to have a negligible packing fraction, and the provisional figure — 6.5 then recorded if corrected for the latest value of  $^{19}\text{F}$  becomes — 4.2.

Direct and much more accurate measurements of the isotopes of silicon have been made by the doublet method.<sup>5</sup>  $^{28}\text{Si}$  was compared with CO and  $^{29}\text{Si}$  with  $^{10}\text{BF}$  with results tabulated on p. 104. Correcting to the latest values of substandards the isotopic weights become  $27.9866 \pm 0.0007$  and  $28.9864 \pm 0.0008$  respectively. These figures combine with those of McKellar to give a chemical atomic weight of 28.125 which suggests that the international one now in use 28.06 is too low.

### 15. Phosphorus.

This element can be conveniently examined by means of its gaseous hydride  $\text{PH}_3$  which gives four lines 31, 32, 33, 34. As these clearly corresponded to P,  $\text{PH}$ ,  $\text{PH}_2$ ,  $\text{PH}_3$  and no others could be seen, it was assumed that phosphorus was a simple element.<sup>6</sup>

In order to determine its packing fraction advantage was taken of the fact that the numerical ratio CO : P is sufficiently close to

<sup>1</sup> Mulliken, *Nature*, **113**, 423; 489, 1924.

<sup>2</sup> Aston, *Phil. Mag.*, **49**, 1198, 1925.

<sup>3</sup> *Phys. Rev.*, **45**, 761, 1934.

<sup>4</sup> Aston, *Proc. Roy. Soc., A*, **132**, 491, 1931.

<sup>5</sup> Aston, *Nature*, **137**, 613; **138**, 1094, 1936.

<sup>6</sup> Aston, *Phil. Mag.*, **40**, 632, 1920.

P : PH<sub>3</sub> to give the small intervals necessary for the application of method III.<sup>1</sup> If the pair CO, P is photographed between the slightly wider pair P, PH<sub>3</sub>, as indicated in Spectrum VIII, Plate VI, the two intervals can both be measured on the same spectrum, though it was found safer to bring them into the same position on the plate by a second exposure.<sup>2</sup> The packing fraction found in this way was — 5·6 which with the correction then in use indicated an atomic weight of 30·978 so much lower than the value 31·02, well established by chemical methods, that heavier isotopes were suggested.<sup>3</sup> On the other hand Ritchie<sup>4</sup> from the density of phosphine found an atomic weight 30·977, and quite recently in revisions by chemical methods Honigschmid<sup>5</sup> has obtained 30·978 and 30·974. There is so far no evidence of any stable isotope except <sup>31</sup>P and a more accurate estimate of its packing fraction has been made by means of the natural doublet <sup>12</sup>C<sup>19</sup>F—<sup>31</sup>P by the writer,<sup>6</sup> with results tabulated on p. 104. Corrected to the latest substandards these give a packing fraction — 5·22 and an isotopic weight 30·9839 ± 0·0005. This corresponds to an atomic weight 30·975, the international one is now 30·98.

### 16. Sulphur.

This element was first investigated by means of its compound sulphur dioxide.<sup>7</sup> Results then obtained are shown in Plate IV, Spectra VII and VIII. Above each is a comparison spectrum taken immediately before the gas was admitted, on the same plate and with approximately the same fields. The lines 32, 33, 34 were clearly due to the introduction of sulphur. Line 32 was certainly due to the element itself, but experience had shown that the oxygen line 16 was almost invariably accompanied by lines 17 and 18 which were certainly due to OH and OH<sub>2</sub>, hence similar hydrides SH and SH<sub>2</sub> were to be expected. The chemical atomic weight 32·06 certainly suggested isotopes of higher mass number, but the apparatus was quite incapable of separating the line due to O<sub>2</sub> from that of a sulphur of mass 32·06 if that existed. Hence it seemed safest to rest content with the certain conclusion that atoms of mass number 32 were present in preponderating proportion. As soon as the second mass spectrograph was found to be capable of resolving doublets such an oxygen, methane, the matter was put to a direct test.<sup>8</sup> Spectra were obtained under conditions such that both O<sub>2</sub> and S must have been present, but the line 32 showed

<sup>1</sup> V. p. 79.

<sup>2</sup> Aston, *Proc. Roy. Soc., A*, **115**, 504, 1927.

<sup>3</sup> Naudé, *Phys. Rev.*, **36**, 346, 1930. <sup>4</sup> *Proc. Roy. Soc., A*, **128**, 578, 1930.

<sup>5</sup> *Zeit. anorg. Chem.*, **235**, 129, 1937; **243**, 355, 1940.

<sup>6</sup> Aston, *Nature*, **138**, 1094, 1936.

<sup>7</sup> Aston, *Phil. Mag.*, **40**, 631, 1920.

<sup>8</sup> Aston, *Proc. Roy. Soc., A*, **115**, 487, 1927.

no signs of doubling. This proved that the atom of  $^{32}\text{S}$  could not have a mass 32.06 so that atoms of higher mass number must be present. Further tests showed that the faint companions 33, 34 (S) ; 49, 50 ( $\text{SO}$ ) ; 65, 66 ( $\text{SO}_2$ ), etc., were present on all spectra, even when the conditions were such as to make the presence of hydrides very unlikely. The intensity relations of the lines were also strongly indicative of true isotopic character. As a final confirmation a negative mass spectrum of  $\text{SO}_2$  was taken by exposing for an hour with both fields reversed. Lines 32, 33, and 34 were all visible and again showed the same intensity relations.

The abundances were roughly estimated as 96 : 1 : 3. Very accurate analyses of sulphur have been recently made by Nier with his precision mass spectrometer<sup>1</sup> in a search for the stable  $^{36}\text{S}$  predicted by Wigner.<sup>2</sup> He obtains evidence for the existence of this and estimates the ratio  $^{32}\text{S} : ^{36}\text{S}$  at  $6000 \pm$  ten per cent. The absence of other isotopes is proved to a very high degree. Nier's figures correspond to the percentage abundances :

Mass number . . . .	32	33	34	36
Abundance . . . .	95.1	0.74	4.2	0.016

The packing fraction of  $^{32}\text{S}$  has been determined by the writer<sup>3</sup> by measurement of the doublet  $^{32}\text{S}-^{18}\text{O}_2$ . The figure obtained was — 5.53 corresponding to an isotopic weight 31.9823  $\pm$  0.0003. Using this and the abundances given the atomic weight of sulphur is identical with that now in use 32.06.

### 17. Chlorine.

During the controversy caused by Soddy's application of his theory of isotopes to ordinary elements, chlorine with its pronounced fractional atomic weight naturally received the greatest attention. Sir J. J. Thomson's abortive attempt to analyse it with his parabola apparatus, and his mistaken conclusion that it was simple have already been mentioned on p. 37.

Spectra indicating that this element was a mixture of isotopes were first obtained by the use of hydrochloric acid gas, but as this was objectionable on account of its action on mercury, phosgene ( $\text{COCl}_2$ ) was substituted.<sup>4</sup> Spectra II, III, and IV, Plate III, are reproduced from one of the plates taken with this gas. Spectrum I is reproduced for comparison, it shows the state of the tube before chlorine compounds were introduced. It will be seen that chlorine is characterized by the appearance of four very definite lines in the previously un-

<sup>1</sup> *Phys. Rev.*, 53, 282, 1938.

<sup>2</sup> *Ibid.*, 51, 947, 1037.

<sup>3</sup> Aston, *Nature*, 138, 1094, 1936; *Proc. Roy. Soc., A*, 163, 391, 1937.

<sup>4</sup> Aston, *Nature*, 104, 393, 1919; *Phil. Mag.*, 39, 620, 1920.

## 17. CHLORINE

occupied space to the right of O<sub>2</sub> (32) : measurement shows these lines to correspond exactly to masses 35, 36, 37, and 38. On Spectrum II, Plate III, taken with a small magnetic field, faint lines will be seen at 17·5 and 18·5. These only appeared when chlorine was introduced, and are certainly second order lines corresponding to 35 and 37. Chlorine is therefore a mixture of isotopes, and two of these have masses 35 and 37. Evidence that <sup>35</sup>Cl and <sup>37</sup>Cl are the main if not the only constituents is given by the strong lines 63 and 65 (Spectrum IV, Plate III), due to CO<sup>35</sup>Cl and CO<sup>37</sup>Cl. The lines 36 and 38 were naturally ascribed to the hydrochloric acids corresponding to <sup>35</sup>Cl and <sup>37</sup>Cl. That this surmise is correct was definitely proved about a year later when the mass spectra of negatively charged rays of chlorine were successfully obtained in the manner described on p. 54. On the negative mass spectra produced in this way only the two chlorine lines 35 and 37 could be distinguished. The property of forming negatively charged ions is a purely chemical characteristic ; that isotopes of the same element should differ radically in it is quite out of the question. It was therefore perfectly certain that the lines 36 and 38 were not, to any sensible extent, due to isotopes of chlorine.

On many of the spectra obtained from chlorine compounds a very faint line is distinguishable at 39. This was regarded as a possible third isotope which would then be an isobar of potassium. Further evidence rendered this conclusion unlikely. During some experiments with tellurium chloride,<sup>1</sup> exceedingly dense lines were obtained at 35, 36, 37, 38, with no vestige of a line at 39. This made it certain that the hypothetical isotope 39 did not exist in any appreciable quantity.

The ratio of abundance of mass numbers 35 and 37 was estimated by photometry as between 3·0 and 3·1.<sup>2</sup> Later Nier and Hanson<sup>3</sup> obtained the more exact figure 3·07 ± 0·03 which was adopted to give the percentages 75·4 and 24·6 in the table. They also showed that 39 was not present to the extent of 1 in 20,000.

The packing fractions of the chlorine isotopes were first measured with the writer's second mass spectrograph by means of artificial doublets.<sup>4</sup> The results indicated — 4·8 and — 5·2 for <sup>35</sup>Cl and <sup>37</sup>Cl respectively. More reliable values were later obtained by measurements of the natural doublets <sup>12</sup>C<sub>3</sub>-H<sup>35</sup>Cl and <sup>12</sup>C<sub>3</sub>H-<sup>37</sup>Cl. This was first done with the writer's third mass spectrograph,<sup>5</sup> and some of the doublets then obtained are shown in Plate VIII. The isotopic weights deduced, given on p. 105, when corrected for Mattauch's values of C

<sup>1</sup> Aston, *Phil. Mag.*, **45**, 943, 1923.

<sup>2</sup> Aston, *Proc. Roy. Soc., A*, **132**, 497, 1931.

<sup>3</sup> *Phys. Rev.*, **50**, 722, 1936.

<sup>4</sup> Aston, *Proc. Roy. Soc., A*, **115**, 487, 1927.

<sup>5</sup> Aston, *Nature*, **138**, 1094, 1936.

and H become 34.9808 and 36.9785 with packing fractions — 5.5 and — 5.8 respectively. Okuda, Ogata, Aoki and Sugawara<sup>1</sup> from measurements of the same doublets deduce values  $34.97903 \pm 0.00038$  and  $36.97786 \pm 0.00036$ . Either pair of values combined with Nier's ratio of abundance give an atomic weight virtually identical with the international figure 35.457 derived from purely chemical data.

### 18. Argon.

Argon was one of the first elements to be analysed.<sup>2</sup> Its lines obtained with the first mass spectrograph are shown in Plate III. As expected from the atomic weight it gave a very strong first order line at 40. Second and third order lines at 20 and  $13\frac{1}{3}$  were observed and owing to the position of the latter in the C<sub>1</sub> group of reference lines the mass of  ${}^{40}\text{A}$  could be fixed with unusual precision. It worked out to be a whole number within 1 part in 1000 and since the density atomic weight was then accepted to be 39.9 search was made for a lighter isotope. This was found to be 36, a very faint line. It was not till 14 years later that Zeeman and de Gier<sup>3</sup> were able to announce a third rare isotope of mass number 38. This was later confirmed by Nier,<sup>4</sup> who also showed the absence of any other isotope to a high degree. The ratio of abundance of the two stronger isotopes was estimated by Vaughan, Williams and Tate<sup>5</sup> as  ${}^{40}\text{A} : {}^{36}\text{A} = 304 \pm 12$ . Later measurements by Nier<sup>6</sup> gave 325, and for the ratio  ${}^{36}\text{A} : {}^{38}\text{A} = 5.1$ . These were adopted in the international table in the form of the following percentages :

Mass number .	36	38	40
Abundance .	0.31	0.06	99.63

Argon was one of the elements examined in the first survey of packing fractions.<sup>7</sup> Its principal isotope was first measured against CO<sub>2</sub> by means of the approximate ratio P : PH<sub>3</sub>. Better results were obtained from its second order line using the more exact ratio  ${}^{40}\text{A}^{++} : \text{O}, \text{CH}_3 : \text{C}$ . The mean value for the packing fraction was — 7.2, giving an isotopic weight 39.971. This figure was supported by the later work of Bainbridge,<sup>8</sup> who gave as a provisional value 39.9724. Experiments with  ${}^{36}\text{A}$  were troublesome owing to its extreme faintness. It was measured by the series  ${}^{36}\text{A} : {}^{40}\text{A} : \text{CO}_2$  and a provisional packing fraction — 6.6 arrived at.

<sup>1</sup> *Phys. Rev.*, **58**, 578, 1940.

<sup>2</sup> Aston, *Nature*, **105**, 8, 1920; *Phil. Mag.*, **39**, 620, 1920.

<sup>3</sup> *Proc. Roy. Acad. Amst.*, **37**, 127, 1934.

<sup>4</sup> *Phys. Rev.*, **49**, 272, 1936; **53**, 282, 1938. <sup>5</sup> *Ibid.*, **46**, 327, 1934.

<sup>6</sup> *Ibid.*, **49**, 272, 1936. <sup>7</sup> Aston, *Proc. Roy. Soc., A*, **115**, 487, 1927

<sup>8</sup> *Phys. Rev.*, **43**, 424, 1933.

With modern high-power instruments greater accuracy was attained. The natural doublet  ${}^{40}\text{A}^{++}$ - ${}^{20}\text{Ne}$  was measured by the writer<sup>1</sup> and gave a packing fraction - 6.15 and isotopic weight  $39.9754 \pm 0.0014$ . Bainbridge and Jordan<sup>2</sup> gave  $39.97580 \pm 0.00031$ , which was subsequently reduced to  $39.97504 \pm 0.00026$ .<sup>3</sup> Mattauch's latest value is  $39.97564 \pm 0.000153$ <sup>4</sup> and a still more recent determination is by Okuda, Ogata, Aoki and Sugawara<sup>5</sup> who from measurements of the doublet  $\text{C}_3\text{H}_4$ - ${}^{40}\text{A}$  obtain  $39.97637 \pm 0.00057$  and from doublet  $\text{C}_3\text{H}_5$ - ${}^{40}\text{A}$   $39.97500 \pm 0.00062$ . No explanation is given for the discrepancy.

The only doublets of  ${}^{36}\text{A}$  measured are  ${}^{36}\text{A}^{++}$ - $\text{OH}_2$ , and  ${}^{36}\text{A}$ - ${}^{12}\text{C}_3$ , used by the writer<sup>6</sup> to check the isotopic weight of  ${}^{12}\text{C}$ . The packing fraction deduced from the first is - 6.10 giving an isotopic weight  $35.978 \pm 0.0010$ .

Combining Nier's abundances with any of the recent values of the isotopic weights of  ${}^{40}\text{A}$  the atomic weight is 39.951 in good agreement with the international value from density determinations of 39.944.

### 19. Potassium.

Anode rays of potassium are easy to produce and the effect due to a small quantity of this element is distinguishable in the early parabola photograph of lithium reproduced in Plate I. Its isotopes were first analysed by the first mass spectrograph<sup>7</sup> and shown to have mass numbers 39 and 41, the former being very much the more abundant. This result was confirmed by Dempster.<sup>8</sup> Potassium had long been known to be feebly radioactive and the work of Hevesy<sup>9</sup> indicated that the property must be due either to isotope 41 or to other undiscovered heavy isotopes. A search by Bainbridge<sup>10</sup> failed to reveal the latter. Later evidence led to the view that the radioactivity must be due to isotope 40 present in small quantity,<sup>11</sup> and this isotope was successfully detected by Nier<sup>12</sup> who estimated its abundance relative to 39 to be 1 in 8600. Brewer<sup>13</sup> confirming this result gave a ratio I in 8300 and from further work<sup>14</sup> has recently come to the conclusion that the abundance of  ${}^{40}\text{K}$  is remarkably constant throughout nature.

The ratio of abundance of the two more abundant isotopes has received much attention. Dempster's original estimate was 18,<sup>15</sup> but

<sup>1</sup> Aston, *Nature*, **137**, 613, 1936.

<sup>2</sup> *Phys. Rev.*, **51**, 385, 1937.

<sup>3</sup> *Rev. Mod. Phys.*, **9**, 370, 1937.

<sup>4</sup> *Zeit. tech. Phys.*, **12**, 578, 1938.

<sup>5</sup> *Phys. Rev.*, **58**, 578, 1940.

<sup>6</sup> Aston, *Nature*, **139**, 922, 1937.

<sup>7</sup> Aston, *Phil. Mag.*, **42**, 436, 1921.

<sup>8</sup> *Phys. Rev.*, **20**, 631, 1922.

<sup>9</sup> V. p. 257.

<sup>10</sup> *J. Franklin Inst.*, **212**, 338, 1931.

<sup>11</sup> Hevesy, *Nature*, **135**, 96, 1935; Newman and Walke, *Ibid.*, 98.

<sup>12</sup> *Phys. Rev.*, **48**, 283, 1935.

<sup>13</sup> *Ibid.*, **48**, 640, 1935.

<sup>14</sup> *Ibid.*, **55**, 669, 1939.

<sup>15</sup> *Ibid.*, **20**, 631, 1922.

Brewer and Kneck, using aluminium silicates of the alkalis, obtained the value  $13.88 \pm 0.4$ .<sup>1</sup> Other values are Nier<sup>2</sup> 13.96, Bondy, Johansen and Popper<sup>3</sup> 16.2, Manley<sup>4</sup> 13.4  $\pm$  0.5, and Bondy and Vanicek<sup>5</sup> 14. Brewer<sup>6</sup> made a very complete examination of the ratio in potassium from various sources. Plant ashes showed a large variation 12.63 to 14.32, minerals rather less 14.11 to 14.6, and samples of sea water were constant at 14.2. The normal constitution of the element potassium may be taken as :

Mass number . . . .	39	40	41
Abundance . . . .	93.4	0.011	6.6

No direct value for the packing fractions of the isotopes of potassium is available though Dempster<sup>7</sup> has examined the position of the second order line of  $^{39}\text{K}$  in the fifth order group of ruthenium. If we assume a value — 6 the atomic weight becomes 39.098, practically identical with the chemical value 39.096.

### 20. Calcium.

This element was first analysed by Dempster, who found it behaved well in his apparatus showing a strong peak at 40 and a weak one at 44.<sup>8</sup> It was examined with the first mass spectrograph<sup>9</sup> by the method of accelerated anode rays and its line 40 shown to be integral. No more work was done on the element until 1934 when, in connection with the problem of the radioactivity of potassium, a more searching analysis was made with the second mass spectrograph and improved anode ray technique.<sup>10</sup> Two new isotopes 42 and 43 were discovered and the constitution of the element estimated by photometry as given below. To test the view that  $^{41}\text{K}$  changing to  $^{41}\text{Ca}$  was responsible for the activity of potassium line 41 was searched for but proved absent to the extent of 1 in 1000. A still more accurate analysis of calcium was made later by Nier<sup>11</sup> using the vapour of the metal in his spectrometer. Two more isotopes 46 and 48 were revealed and the abundances measured with the following results. The absence of other mass numbers was proved to a very high degree.

Mass number .	40	42	43	44	46	48
Abundance (1)	96.76	0.77	0.17	2.30	—	—
(2)	96.97	0.64	0.145	2.06	0.0033	0.185

(1) Aston, 1934; (2) Nier, 1938.

<sup>1</sup> *Phys. Rev.*, **46**, 894, 1934.

<sup>2</sup> *Ibid.*, **48**, 283, 1935.

<sup>3</sup> *Zeit. Phys.*, **95**, 46, 1935.

<sup>4</sup> *Phys. Rev.*, **49**, 921, 1936.

<sup>5</sup> *Zeit. Phys.*, **101**, 186, 1936.

<sup>6</sup> *J. Amer. Chem. Soc.*, **58**, 365, 1936.

<sup>7</sup> *Phys. Rev.*, **53**, 74, 1938.

<sup>8</sup> *Ibid.*, **20**, 633, 1922.

<sup>9</sup> Aston, *Phil. Mag.*, **47**, 394, 1924.

<sup>10</sup> Aston, *Nature*, **133**, 684, 1934; *Proc. Roy. Soc., A*, **149**, 396, 1935.

<sup>11</sup> *Phys. Rev.*, **53**, 282, 1938.

No data are yet available on the packing fractions of the calcium isotopes, but if we assume a value — 6 the atomic weight becomes identical with the chemical value 40.08.

### 21. Scandium.

This was the first of the rare earth elements to give results with the mass spectrograph. In the early work<sup>1</sup> an anode containing the fluoride was used and only one line at 45 was detected, but as it was very faint this did not disprove the presence of isotopes suggested by the chemical atomic weight of 45.1. Using the second mass spectrograph, these experiments have been repeated<sup>2</sup> with an anode consisting of scandium fluoride, from the same sample as that originally used, and a little potassium bromide. The scandium line was obtained at once and by exposing for over 1 hour the intensity of this was increased to such a value that any other isotope present to the extent of 3 per cent. could have been detected. None was, which proves that scandium is simple to that degree.

No measurement of the packing fraction of  $^{45}\text{Sc}$  are available but disintegration results suggest about — 6.5, hence correcting for scale the atomic weight is  $44.96 \pm 0.05$  which suggests that the chemical value 45.10 needs revision.

### 22. Titanium.

The first attempts on this metal were made with its volatile chloride but failed, for, owing to the violent action of this compound on parts of the apparatus, the mass spectra were too complex for identification.<sup>3</sup> In a later experiment with accelerated anode rays<sup>4</sup> it was possible to conclude that the principal isotope was of mass number 48, the presence of others being doubtful. It was not until ten years later that conclusive mass spectra were obtained.<sup>5</sup> The strong line 48 was found flanked by weak symmetrical pairs of satellites 46, 47, 49, 50 the whole forming a group of very striking appearance. The relative abundance was estimated by photometry as below. This constitution was confirmed later by Nier<sup>6</sup> who made more accurate measurements of abundance :

Mass number	.	.	46	47	48	49	50
Abundance (1)	.	.	8.5	7.8	71.3	5.5	6.9
(2)	.	.	7.94	7.75	73.45	5.52	5.34

(1) Aston, 1935; (2) Nier, 1938.

<sup>1</sup> Aston, *Phil. Mag.*, **47**, 396, 1924.

<sup>2</sup> Aston, *Proc. Roy. Soc., A*, **134**, 571, 1932.

<sup>3</sup> Aston, *Phil. Mag.*, **45**, 937, 1923. <sup>4</sup> *Ibid.*, **47**, 397, 1924.

<sup>5</sup> Aston, *Nature*, **133**, 684, 1935; *Proc. Roy. Soc., A*, **149**, 396, 1935.

<sup>6</sup> *Phys. Rev.*, **53**, 282, 1938.

The packing fraction of  $^{48}\text{Ti}$  has been measured by Dempster<sup>1</sup> as — 7.22 by direct comparison of its triply charged line with  $^{16}\text{O}$  (*v.* Plate IX), and by the writer<sup>2</sup> as — 7.24 by comparison of its doubly charged line with  $^{12}\text{C}_2$ . With Mattauch's value of  $^{12}\text{C}$  this becomes — 7.0. With Nier's abundances these packing fractions give an atomic weight 47.88 in good agreement with the chemical value 47.90.

### 23. Vanadium.

This element was investigated during the first set of experiments with accelerated anode rays.<sup>3</sup> An anode consisting of vanadium chloride mixed with lithium iodide was used. A single line appeared in the expected position corresponding to mass number 51. This was compared with  $^{39}\text{K}$  on the one side and with  $^{56}\text{Fe}$  on the other and appeared integral with them to the accuracy of measurement. No further data are available from mass spectra but indirect evidence from disintegration experiments supports the view that vanadium is simple, and indicates a packing fraction of about — 8 giving a chemical atomic weight virtually identical with the international value 50.95.

### 24. Chromium.

The first successful experiment with this element was made by the use of an anode containing halides of chromium.<sup>4</sup> One line only appeared at 52 and as this agreed exactly with the chemical atomic weight chromium was regarded as a simple element. The application<sup>5</sup> of the more powerful and convenient method of the ordinary discharge tube was later made possible through the preparation of a suitable volatile compound, the hexacarbonyl. The vapour pressure of this white crystalline solid is appreciable at ordinary temperature but not high enough to give a sufficient flow through the customary fine glass "leak." The latter was therefore not used, but instead the vapour was allowed to diffuse directly into the discharge bulb with no more obstruction than two stopcocks and a few centimetres of narrow bore tubing. Even with this arrangement the rate of diffusion was so low that no difficulty was experienced in keeping the pressure down by slow pumping.

The beams of rays obtained were vastly more intense than those given by the anode rays and it was soon realized that chromium had four isotopes, 50, 52, 53, 54, of which 52 was much the strongest. It was impossible to hold the discharge constant for any considerable length of time and the relative abundance was determined by the

<sup>1</sup> *Phys. Rev.*, **53**, 68, 1938.

<sup>2</sup> Aston, *Nature*, **141**, 1096, 1938.

<sup>3</sup> Aston, *Phil. Mag.*, **47**, 397, 1924.

<sup>4</sup> Aston, *Ibid.*, **47**, 397, 1924.

<sup>5</sup> Aston, *Proc. Roy. Soc., A*, **130**, 306, 1931.

method of intermittent exposures, with results given below. More accurate electrometric measurements have been made recently by Nier,<sup>1</sup> who also proved the absence of other mass numbers to a very high degree.

Mass number	.	50	52	53	54
Abundance (1)	.	4.9	81.6	10.4	3.1
(2)	.	4.49	83.78	9.43	2.30

(1) Aston, 1931; (2) Nier, 1939.

The writer's observations in 1931 indicated a large negative packing fraction for  $^{52}\text{Cr}$  of the order of — 10. A much more reliable determination has been made by measuring the doublet  $\text{CH}_3\text{Cl}-^{52}\text{Cr}$  to be 0.0479 unit.<sup>2</sup> Using the latest values of the reference elements concerned this gives an isotopic weight of  $^{52}\text{Cr}$  to be  $51.9582 \pm 0.0008$  corresponding to a packing fraction of — 8.0. Combining this with Nier's abundances the atomic weight of the element becomes 52.00 in good agreement with the international chemical value 52.01.

### 25. Manganese.

The first results recorded for manganese are those obtained with the first mass spectrograph by the method of accelerated anode rays. Manganese fluoride and lithium iodide were used in the anode mixture,<sup>3</sup> and one line only was observed at 55 which appeared integral with the neighbouring line of  $^{56}\text{Fe}$ . The conclusion then made that manganese was a simple element was in good accord with the chemical atomic weight, and was confirmed to a very high degree indeed by the work of Sampson and Bleakney.<sup>4</sup> If we assume a probable packing fraction of about — 8 the atomic weight becomes identical with the chemical figure 54.93.

### 26. Iron.

This element was first analysed by means of its volatile carbonyl<sup>5</sup> and the spectra indicated that its principal isotope was of mass number 56. They also showed a faint line 54, the origin of which was doubtful owing to the presence of compounds. The existence of the rarer isotope 54 was definitely proved later by means of accelerated anode rays,<sup>6</sup> and its abundance estimated at about 5 per cent.

Later work on the carbonyl with the second mass spectrograph<sup>7</sup> revealed a third isotope 57, and enabled the abundances to be estimated photometrically as given below. A faint line 58 was present but

<sup>1</sup> *Phys. Rev.*, **55**, 1143, 1939.    <sup>2</sup> Aston, *Nature*, **141**, 1096, 1938.

<sup>3</sup> Aston, *Phil. Mag.*, **47**, 396, 1924.    <sup>4</sup> *Phys. Rev.*, **50**, 732, 1936.

<sup>5</sup> Aston, *Phil. Mag.*, **45**, 940, 1923.    <sup>6</sup> Aston, *Ibid.*, **49**, 1198, 1925.

<sup>7</sup> Aston, *Proc. Roy. Soc., A*, **149**, 396, 1935.

regarded as doubtful owing to the possible presence of nickel. By analysis of iron carbonyl with the parabola apparatus de Gier and Zeeman<sup>1</sup> identified 58 as a rare isotope and gave an estimate of its abundance as 0·5 per cent., but did not measure the abundances of the other isotopes. <sup>58</sup>Fe was confirmed by Dempster,<sup>2</sup> and was included in the table of 1936. Accurate electrometric measurements have been recently made by Nier,<sup>3</sup> and percentage abundances calculated from his ratios adopted in the table of 1940 as given below. Since then Valley and Anderson<sup>4</sup> have analysed terrestrial and meteoric iron electrometrically. Their results, given on p. 214, are nearly identical with Nier's, and those for terrestrial iron transformed into percentages are given in the following table.

Mass number .	. .	54	56	57	58
Abundance (1)	. .	6·5	90·7	2·8	—
(2)	. .	6·0	91·6	2·1	0·28
(3)	. .	5·83	91·7	2·16	0·31

(1) Aston, 1935 ; (2) Nier, 1939 ; (3) Valley, 1941.

The packing fractions of two of the isotopes of iron have been measured by Dempster.<sup>5</sup> By comparing the fourth order line of <sup>58</sup>Fe with <sup>14</sup>N he gets  $-7\cdot1 \pm 0\cdot4$ , and from the position of <sup>54</sup>Fe between the second order lines of silver  $-7\cdot4 \pm 0\cdot8$ . More recently Okuda, Ogata, Aoki and Sugawara<sup>6</sup> from the doublet C<sub>4</sub>H<sub>8</sub>—<sup>56</sup>Fe get  $-7\cdot7$ , in better agreement with the neighbouring elements Cr and Ni, and give the isotopic weight provisionally as  $55\cdot9572 \pm 0\cdot0012$ . With Okuda's packing fraction either Nier's or Valley's abundances give an atomic weight virtually identical with the present international one 55·85.

### 27. Cobalt.

The early work on this element was done with the first mass spectrograph by the method of accelerated anode rays.<sup>7</sup> Anhydrous cobaltous chloride was used in the anode and a single line was obtained corresponding to mass number 59. This result together with a chemical atomic weight and the probable high negative packing fraction all agreed with the conclusion that cobalt was simple. Later, however, a search by Sampson, Ridenour and Bleakney<sup>8</sup> revealed a rare constituent 57 estimated by them to be  $600 \pm 20$  times less abundant than 59. This they confirmed by later work.<sup>9</sup> It is to be

<sup>1</sup> Proc. Roy. Acad. Amst., 38, 959, 1935.

<sup>2</sup> Phys. Rev., 50, 98, 1936.

<sup>3</sup> Ibid., 55, 1143, 1939.

<sup>4</sup> Ibid., 59, 113, 1941.

<sup>5</sup> Ibid., 53, 64, 1938.

<sup>6</sup> Ibid., 58, 578, 1940.

<sup>7</sup> Aston, Phil. Mag., 47, 395, 1924.

<sup>8</sup> Phys. Rev., 50, 382, 1936.

<sup>9</sup> Sampson and Bleakney, Ibid., 732, 1936.

noted that since stable  $^{57}\text{Fe}$  is well established the existence of a stable  $^{57}\text{Co}$  is against the statistical rule in respect to the odd numbered isobars of adjacent elements,<sup>1</sup> but it is not the only exception.

No measurements of the packing fraction of cobalt have been made, but if we assume it to be between — 7 and — 8 the atomic weight is 58.93 in good agreement with the chemical value 58.94.

### 28. Nickel.

Nickel received attention early in the history of positive rays as it is one of those elements whose atomic weight is out of order in the periodic table; its atomic weight 58.69 should be greater, not less than that of cobalt 58.94. It is amenable to treatment in the ordinary discharge tube, for it forms an easily vaporizable carbonyl compound  $\text{Ni}(\text{CO})_4$ . Unfortunately this is rapidly decomposed by the electric discharge, so that in the early experiments made by Sir J. J. Thomson the walls of the discharge bulb became coated with a black deposit of the metal; it was impossible to maintain a steady discharge for a sufficient time, and no satisfactory parabola corresponding to the element could be obtained.

Later by the use of abnormally high current intensities in the discharge it was found possible to overcome these difficulties to some extent and to obtain a mass spectrum from a mixture of nickel carbonyl and carbon dioxide.<sup>2</sup> This showed two lines, the stronger at 58 and the weaker at 60, with a ratio of intensity of about 2 to 1.

A more thorough examination was made with the second mass spectrograph again using the carbonyl.<sup>3</sup> Several new lines were detected of which 61 and 62 were regarded as certainly isotopes, lines at 56 and 64 as doubtful owing to the possible presence of  $^{56}\text{Fe}$  and  $\text{SO}_2$ . The relative abundance of the four mass numbers was estimated by photometry as given below. The parabola analysis of nickel carbonyl by de Gier and Zeeman<sup>4</sup> confirmed line 64 as an isotope, but failed completely to detect line 61. Dempster<sup>5</sup> using nickel metal of exceptional purity describes lines 61 and 64 as being of roughly equal intensity in all his spectra (*v. Plate IX.*) Recently Lub<sup>6</sup> has repeated the parabola experiments, this time getting line 61 but ten times weaker than line 64. This fallacious result has already been fully discussed.<sup>7</sup> Comparison of these two lines by a null electric method in an analysis of nickel by Straus<sup>8</sup> shows that 61 is 1.3 times

<sup>1</sup> V. p. 204.

<sup>2</sup> Aston, *Phil. Mag.*, **45**, 936, 1923.

<sup>3</sup> Aston, *Proc. Roy. Soc., A*, **149**, 396, 1935.

<sup>4</sup> *Proc. Roy. Acad. Amst.*, **38**, 810, 1935.

<sup>5</sup> *Phys. Rev.*, **50**, 98, 1936.

<sup>6</sup> *Ibid.*, **42**, 253, 1939.

<sup>7</sup> V. p. 89.

<sup>8</sup> *Phys. Rev.*, **59**, 102; **430**, 1941.

as abundant as 64, a ratio confirmed by the still more recent measurements of Valley<sup>1</sup> which were made by the standard spectroscopic method. The estimates of the percentage abundance of nickel isotopes are :

Mass number	.	.	58	60	61	62	64
Abundance (1)	.	.	67.5	27.0	1.7	3.7	?
(2)	.	.	62.8	29.5	1.7	4.7	1.3
(3)	.	.	67.4	26.7	1.2	3.8	0.88

(1) Aston, 1935; (2) Straus, 1941; (3) Valley, 1941.

The first estimate of the packing fraction of nickel was made by the writer<sup>2</sup> by using artificial doublets given by the approximate ratios C : CH<sup>4</sup> and CO<sub>2</sub> : <sup>58</sup>Ni. A provisional value of about — 10 was suggested. Later these measurements were repeated with his third, more powerful, instrument<sup>3</sup> when a value — 8.35 was obtained, which becomes about — 8.5 with the later value of carbon. Quite recently Okuda, Ogata, Kuroda, Shima and Shindo<sup>4</sup> have measured the packing fractions of five nickel lines against hydrocarbons with a double focusing mass spectrograph and using Schumann plates. They give the following figures : <sup>58</sup>Ni—6.97, <sup>60</sup>Ni—8.37, <sup>61</sup>Ni—7.5, <sup>62</sup>Ni—8.14 and <sup>64</sup>Ni—8.22. A difference of packing fraction of 1.4 of a unit between the two strongest isotopes is an unexpected result of great interest, if it is confirmed. The combination of these results with the abundances given by Valley gives an atomic weight 58.71 in fair agreement with the international chemical one 58.69.

### 29. Copper.

Data on this element are unusually meagre. Results obtained by Dempster<sup>5</sup> suggesting that it had three isotopes of even mass number were spurious and probably due to traces of zinc.<sup>6</sup> Reliable mass spectra were first obtained by the method of accelerated anode rays.<sup>7</sup> An anode of cuprous chloride, lithium iodide and rubidium chloride was used. The last salt was added to provide reference lines. The effects obtained from copper were faint, but conclusive, as both in intensity and position its lines 63 and 65 appeared in accordance with statistical considerations.<sup>8</sup> They were measured against <sup>85</sup>Rb on one side and <sup>56</sup>Fe on the other, and showed no measurable deviation from the whole number rule. The ratio of their intensities was about 5 : 2 in reasonable agreement with the chemical atomic weight 63.57.

<sup>1</sup> *Phys. Rev.*, **59**, 771, 1941.

<sup>2</sup> Aston, *Nature*, **120**, 956, 1927.

<sup>3</sup> Aston, *Ibid.*, **141**, 1096, 1938.

<sup>4</sup> *Phys. Rev.*, **59**, 104, 1941.

<sup>5</sup> *Nature*, **112**, 7, 1923.

<sup>6</sup> Aston, *Ibid.*, **112**, 162, 1923.

<sup>7</sup> Aston, *Phil. Mag.*, **47**, 395, 1924.

<sup>8</sup> V. p. 204.

Using his "hot spark" method Dempster<sup>1</sup> has photographed the fourth order lines of copper, and from the position of the  $^{16}\text{O}$  line between them has estimated their mean packing fraction as  $- 6.9 \pm 0.2$ . No accurate measurements have yet been made on the relative abundance of the two isotopes.

### 30. Zinc.

This metal was first investigated by Dempster.<sup>2</sup> The results were at first inconsistent, but curves obtained from a calcium anode to which had been added a little zinc gave sharper bundles of rays and were regarded as satisfactory. The form of the curve is shown in Fig. 36.

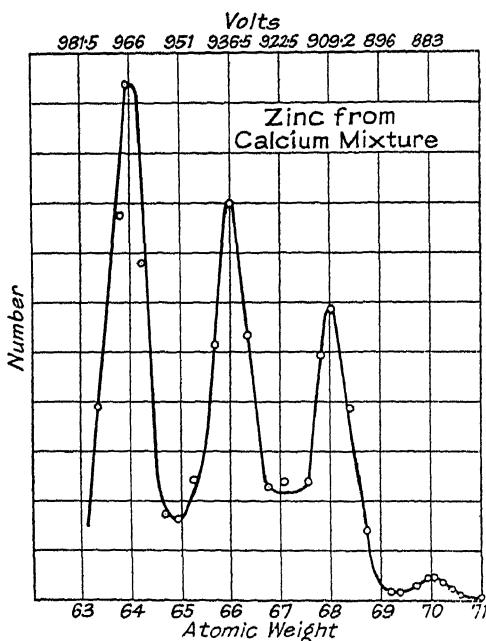


FIG. 36.—Dempster's Curve for Zinc.

The values for the mass numbers were obtained by direct comparison with the calcium line at 40; they indicated that zinc consisted of three strong isotopes 64, 66, 68 and a fourth faint one 70. The probability of an unresolved isotope 67 was suggested.

Early attempts to confirm this result on the first mass spectrograph by the use of zinc methyl failed to show any zinc lines at all.<sup>3</sup> Later

<sup>1</sup> *s. Rev.*, 53, 64, 1938.

<sup>2</sup> Dempster, *Ibid.*, 20, 633, 1922.

<sup>3</sup> Aston, *Phil. Mag.*, 45, 937, 1923.

experiments with the second mass spectrograph<sup>1</sup> made it clear that the secret of obtaining strong zinc lines was to have nothing but the vapour of zinc methyl present. The presence of other elements more easily ionized or capable, from any other cause, of carrying the current more easily seems to act adversely. Doubtless the many earlier failures to get zinc lines were largely due to the presence of mercury. The low ionization potential and abnormally great "current carrying" power of this element appear to enable it to suppress the mass spectrum of zinc entirely, although the partial pressure of the latter is far the greater.

The mass spectra obtained not only showed the lines found by Dempster, and confirmed that at 67, but there were in addition lines at 65 and 69, both stronger than that at 70. As these showed no variation in their intensity they were taken to be genuine isotopes and the relative abundances of the group worked out by the method of intermittent exposures, were found to agree exactly with the chemical atomic weight.

Later, however, Bainbridge,<sup>2</sup> by the use of his velocity selector apparatus<sup>3</sup> and metallic zinc vapour as a source of ions, obtained results which proved beyond question that isotopes 65 and 69 are not present to an appreciable extent, even compared with 70, in the mass rays of zinc. One of the spectra obtained by Bainbridge, is reproduced in Plate VI. It is clear that the lines 65 and 69 were due to the hydrides of the abundant isotopes 64 and 68. An inspection of the relative intensities of the lines shows that these are in exact accord with the assumption that a monohydride corresponding to 5·2 per cent. of each isotope was present. Correcting the original figures for this amount of hydride gave the percentage abundances stated below. Stevinkel and Svensson<sup>4</sup> advanced evidence from optical band spectra indicating that mass numbers 63 and 65 existed and were present in greater abundance than 70 in zinc, but Nier's electrometric analysis<sup>5</sup> provided figures for the abundance of the five isotopes agreeing well with that already obtained, and proving the absence of any others to a very high degree. The percentages for zinc are :

Mass number .	64	66	67	68	70
Abundance (1) .	50·4	27·2	4·2	17·8	0·4
(2) .	50·9	27·3	3·9	17·4	0·5

(1) Aston, 1932; (2) Nier, 1936.

By the use of the carbon molecular lines a provisional value of 9·9 for the packing fraction of <sup>64</sup>Zn was obtained with the writer's

<sup>1</sup> Aston, *Proc. Roy. Soc., A*, **130**, 303, 1931.

<sup>2</sup> Bainbridge, *Phys. Rev.*, **39**, 847, 1932. <sup>3</sup> V. p. 84.

<sup>4</sup> *Nature*, **135**, 955, 1935.

<sup>5</sup> *Phys. Rev.*, **49**, 272; **50**, 1043, 1936.

second mass spectrograph,<sup>1</sup> but this is certainly too large a negative value. Dempster has compared the lines of zinc with those of sodium and silver<sup>2</sup> and deduces for  $^{64}\text{Zn}$  a value  $- 6.9 \pm 0.8$ , for  $^{66}\text{Zn} - 7.4 \pm 0.8$  and for the mean of  $^{68}\text{Zn}$  and  $^{70}\text{Zn} - 6.6 \pm 0.6$ . If we assume a value  $- 7$  the atomic weight is 65.34 as compared with the international chemical one 65.38.

### 31. Gallium.

After a failure to obtain the lines of the element from its volatile chloride it was successfully analysed by the method of accelerated anode rays<sup>3</sup> the anode containing the fluoride made by the action of hydrofluoric acid on the pure hydride. The results were faint but gave satisfactory proof of the presence of two isotopes 69 and 71. The intensities of the two lines agreed well with the chemical atomic weight 69.72.

The analysis was repeated under better conditions with the second mass spectrograph.<sup>4</sup> and the percentage abundance measured photometrically as 61.5 and 38.5 respectively. Sampson and Bleakney<sup>5</sup> with their spectrometer obtained percentages 61.2 and 38.8, which were adopted in the table. No accurate measurement of the packing fraction of gallium has been made, though Dempster<sup>6</sup> has compared its lines with those of palladium finding a difference of about 1.5 units. If we assume a value  $- 7$  the atomic weight is 69.73 in excellent agreement with the international value 69.72.

### 32. Germanium.

The first investigation of germanium was made by accelerated anode rays using a compound resulting from the action of hydrofluoric acid on the oxide. Three lines were detected of mass numbers 70, 72, 74.<sup>7</sup> A more searching analysis was made with the second mass spectrograph using the volatile alkyl compounds in the ordinary discharge. This showed eight lines 70 . . . 77 of which 71, 75 and 77 were weak, but all were assumed to be isotopes. The relative intensities of the group were determined by photometry. Later Bainbridge<sup>8</sup> examined germanium by means of its bromide and iodide. The spectra he obtained, one of which is reproduced in Plate VI, make it quite clear that the lines at 71, 75 and 77 were due to hydrides.

<sup>1</sup> Aston, *Proc. Roy. Soc., A*, **130**, 304, 1931.      <sup>2</sup> *Phys. Rev.*, **53**, 64, 1938.

<sup>3</sup> Aston, *Nature*, **112**, 449, 1923; *Phil. Mag.*, **47**, 397, 1924.

<sup>4</sup> Aston, *Proc. Roy. Soc., A*, **149**, 396, 1935.

<sup>5</sup> *Phys. Rev.*, **50**, 456, 1935.      <sup>6</sup> *Ibid.*, **53**, 64, 1938.

<sup>7</sup> Aston, *Nature*, **111**, 771, 1923; *Phil. Mag.*, **47**, 394, 1924.

<sup>8</sup> *Phys. Rev.*, **43**, 1056, 1933.

Making the appropriate corrections to the writer's figures for intensity we obtain the following percentages :

Mass number	70	72	73	74	76
Abundance	21.2	27.3	7.9	37.1	6.5

No measurements have yet been made on the packing fraction of the germanium isotopes. If we assume a mean value — 7 the atomic weight is 72.59 identical with the most recent chemical value obtained by Honigschmid and Wintersberger.<sup>1</sup> The international figure is 72.60.

### 33. Arsenic.

This element was examined with the first mass spectrograph by means of its gaseous hydride  $\text{AsH}_3$ .<sup>2</sup> The spectrum obtained, shown in Spectrum IX, Plate IV, was similar to that obtained with phosphorus, so it was concluded to be a simple element of mass number 75. This has been confirmed to a very high degree indeed by the more recent quantitative work of Nier.<sup>3</sup>

The packing fraction of  $^{75}\text{As}$  was compared with that of the Br lines by the method of series shift<sup>4</sup> and the difference estimated to be 0.2 unit.<sup>5</sup> With the latest value for Br this gives — 7.2 for  $^{75}\text{As}$ . Correcting to the chemical scale the atomic weight is 74.925. The present chemical figure is 74.91.

### 34. Selenium.

Early attempts to analyse this element by means of its gaseous hydride were completely unsuccessful,<sup>6</sup> but by vaporizing the element itself in the discharge tube conclusive results were at once obtained.<sup>7</sup> The mass spectrum was characterized by five strong lines 76, 77, 78, 80, 82 and a faint sixth 74. The true isotopic nature of this group was beautifully brought out by its repetition at a position 12 units higher on the mass scale due to CSe and 28 units higher due to COSe. The evidence of the isotopic constitution of selenium was therefore exceptionally definite and trustworthy. The relative abundance of the selenium isotopes was later determined by the photometry of its lines obtained by means of the second mass spectrograph, using the vapour as before. The following figures were obtained :

Mass number	74	76	77	78	80	82
Abundance	0.9	9.5	8.3	24.0	48.0	9.3

The value for 76 is suspect, as almost all mass spectra taken in

<sup>1</sup> *Zeit. anorg. Chem.*, **227**, 17, 1936.

<sup>2</sup> Aston, *Phil. Mag.*, **40**, 632, 1920. <sup>3</sup> *Phys. Rev.*, **52**, 933, 1937.

<sup>4</sup> V. p. 78.

<sup>5</sup> Aston, *Proc. Roy. Soc., A*, **115**, 487, 1927.

<sup>6</sup> Aston, *Phil. Mag.*, **42**, 140, 1921.

<sup>7</sup> *Ibid.*, **45**, 941, 1923.

this region with an ordinary discharge show traces of a line at this point. Its origin is unknown and may be  $\text{CS}_2$ . Other possibilities are  $\text{CO}_2\text{S}$ ,  $^{28}\text{SiOS}$  or  $^{28}\text{SiO}_3$ . There is, however, no doubt that the intensity from this unknown source cannot be more than a very small fraction of the total intensity of line 76 when plenty of selenium vapour is present. These figures indicated a chemical atomic weight considerably less than 79·2, the one in use at the time, and a revision made by Honigschmid<sup>1</sup> gave a value 78·962 in good accord with the mass spectrum results. The six isotopes of selenium were confirmed by Bainbridge,<sup>2</sup> who also proved no trace of 79 and 81 predicted by Johnson.<sup>3</sup>

An estimate of the packing fraction of the strongest lines of selenium was made by introducing bromine into the discharge and examining the series of lines 78, 79, 80, 81 by the method of series shift.<sup>4</sup> The results indicated negative values rather less than those of bromine.<sup>5</sup> If we use the latest values for bromine the packing fractions of  $^{78}\text{Se}$  and  $^{80}\text{Se}$  become — 6·4 and — 6·1 respectively, and the atomic weight 78·95, virtually identical with the international chemical one 78·96.

### 35. Bromine.

The early results with this element were definite and easy to interpret.<sup>6</sup> Its chemical combining weight is known with great certainty, and is very nearly the whole number 80. It was rather a surprise, therefore, that it should give a mass spectrum which showed it to consist of a mixture of two isotopes in practically equal proportions. Methyl bromide was used for the experiments, and one of the results is reproduced in Plate IV, Spectrum VI. The characteristic group consists of four lines at 79, 80, 81, and 82. 79 and 81, apparently of equal intensity, are much the stronger pair, and are obviously due to elementary bromines. This result is practically confirmed by second order lines at 39·5 and 40·5, too faint to reproduce, but easily seen and measured on the original negative. The fainter pair, 80 and 82, are the expected lines of the two corresponding hydrobromic acids.

Throughout the earlier work no certain difference of intensity could be observed between the two lines, even when photometry was applied.<sup>7</sup> Still more delicate measurements applied by Blewett<sup>8</sup> show the lighter isotope to be slightly more abundant, the percentages

<sup>1</sup> *Naturwiss.*, **35**, 659, 1932.

<sup>2</sup> *Phys. Rev.*, **43**, 1056, 1933.

<sup>3</sup> *J. Amer. Chem. Soc.*, **54**, 824, 1932.

<sup>4</sup> V. p. 78.

<sup>5</sup> Aston, *Proc. Roy. Soc., A*, **132**, 487, 1931.

<sup>6</sup> Aston, *Phil. Mag.*, **40**, 631, 1920.

<sup>7</sup> Aston, *Proc. Roy. Soc., A*, **132**, 489, 1931.

<sup>8</sup> *Phys. Rev.*, **49**, 900, 1935.

being 50·6 and 49·4 respectively. Blewett also proved the absence of any other isotope to a high degree.

The first measurements of the packing fractions of the bromine isotopes were made with the second mass spectrograph.<sup>1</sup> Some of the spectra used are reproduced in Plate V. The values, obtained by artificial doublets, were — 9·0 and — 8·6 for lines 79 and 81 respectively. Recently more reliable figures, — 7·4 for each isotope, have been obtained<sup>2</sup> by measurement of the natural doublet given by triply charged <sup>79</sup>Br and quintuply charged <sup>132</sup>Xe, the difference in mass between the bromines having been previously determined.<sup>3</sup> Using this value the atomic weight is 79·908 in good accord with the international chemical one 79·916.

### 36. Krypton.

This was the first element shown to be highly complex. Its sixfold group of lines, reproduced in the second and third orders was one of the most striking phenomena disclosed in the early work with the first mass spectrograph.<sup>4</sup> One of the spectra then obtained is shown in Plate III. The proof that the isotopes had whole-number masses, was easy, for their second order lines could be compared with argon, already measured, and those of the third order with CO. Later work by Bainbridge<sup>5</sup> failed to reveal any other isotopes. The relative abundance of the isotopes of krypton was first measured by photometry<sup>6</sup> as has been fully described in Chapter IX. More accurate figures have been since obtained by Nier<sup>7</sup> with his precision mass spectrometer. He also proved the absence of other mass numbers to a very high degree. The constitution of krypton is :

Mass number . . . . .	78	80	82	83	84	86
Abundance (1) . . . . .	0·42	2·45	11·79	11·79	56·85	16·70
(2) . . . . .	0·35	2·01	11·53	11·53	57·11	17·47

(1) Aston, 1930; (2) Nier, 1937.

During the first survey of packing fractions<sup>8</sup> that of <sup>86</sup>Kr was estimated at — 8·2 by the comparison of its second order line with that of CO<sub>2</sub>. Those of the other isotopes were then evaluated by the method of series shift illustrated in Plate VI, Spectrum XI, which showed them to form a very uniform series. Much more reliable values have been obtained by the writer with his second order focusing

<sup>1</sup> Aston, *Proc. Roy. Soc., A*, **115**, 487, 1927.

<sup>2</sup> Aston, *Nature*, **141**, 1096, 1938. <sup>3</sup> Aston, *Ibid.*, **137**, 357, 1936.

<sup>4</sup> Aston, *Ibid.*, **105**, 8, 1920.

<sup>5</sup> *Phys. Rev.*, **43**, 1056, 1933.

<sup>6</sup> Aston, *Proc. Roy. Soc., A*, **126**, 511, 1930.

<sup>7</sup> *Phys. Rev.*, **52**, 933, 1937.

<sup>8</sup> Aston, *Proc. Roy. Soc., A*, **115**, 487, 1927.

instrument,<sup>1</sup> by the use of the beautiful series of natural doublets formed by the second order lines of the even mass numbers of krypton, and those of the C<sub>3</sub> group, some of which are shown in Plate VIII. The doublet at 40 could not be used for this owing to the possible presence of argon. The results then deduced are given on p. 105. If Mattauch's values for carbon and hydrogen are used the isotopic weights of isotopes 78, 82, 84 and 86 are 77.9448, 81.9388, 83.9380 and 85.9384 respectively. Using these figures combined with Nier's abundances the chemical atomic weight works out to be 83.817. The international one based on density determinations is 83.7.

### 37. Rubidium.

This element was analysed by the first mass spectrograph during the early experiments with anode rays.<sup>2</sup> It gave two lines 85 and 87 and photometric measurements<sup>3</sup> indicated that the lighter was the more abundant in the ratio 3 : 1. Brewer and Kneck<sup>4</sup> using artificial aluminium silicates and a Dempster type apparatus obtained a ratio  $2.59 \pm 0.04$ . Bondy, Johannsen and Popper<sup>5</sup> got 2.68. Nier<sup>6</sup> proved the absence of other isotopes to a very high degree and estimated the ratio as  $2.68 \pm 0.02$ . He concluded that the natural radioactivity of the element was due to isotope 87. This was confirmed by Hemmendinger and Smythe<sup>7</sup> and Walcher.<sup>8</sup> Further estimates of the ratio of abundance of the isotopes have been made by Brewer<sup>9</sup> who finds some variation and gives a range of 2.59–2.61. The international figures for the percentages of the isotopes are 72.8 and 27.2 based on Nier's ratio. No measurements on packing fraction have been made, but if we assume a value — 7 the atomic weight is 85.46 in good agreement with the chemical value 85.48.

### 38. Strontium.

In the first investigations of strontium by accelerated anode rays various halides were used, but only one line at 88 could be detected.<sup>10</sup> Further work revealed a fainter component 86.<sup>11</sup> Later the high resolving power of the second mass spectrograph and improved conditions of vacuum enabled a more searching analysis to be made.<sup>12</sup>

<sup>1</sup> Aston, *Nature*, **140**, 149, 1937.      <sup>2</sup> Aston, *Phil. Mag.*, **42**, 436, 1921.

<sup>3</sup> Aston, *Proc. Roy. Soc., A*, **134**, 575, 1932.

<sup>4</sup> *Phys. Rev.*, **46**, 894, 1934.      <sup>5</sup> *Zeit. Phys.*, **95**, 46, 1935.

<sup>6</sup> *Phys. Rev.*, **49**, 272; **50**, 1041, 1936.

<sup>7</sup> *Ibid.*, **51**, 1052, 1087.      <sup>8</sup> *Phys. Zeit.*, **38**, 961, 1937.

<sup>9</sup> *J. Amer. Chem. Soc.*, **60**, 691, 1938.

<sup>10</sup> Aston, *Phil. Mag.*, **47**, 394, 1924.      <sup>11</sup> *Ibid.*, **49**, 1192, 1925.

<sup>12</sup> Aston, *Proc. Roy. Soc., A*, **134**, 573, 1932.

Using an anode containing a mixture of  $\text{SrI}_2$  and  $\text{LiBr}$  the strong component 88 and weak companion 86 were confirmed and in addition a third isotope 87 was discovered. The relative abundances were roughly estimated by photometry. The presence of a still rarer isotope 84 was revealed by the work of Blewett and Sampson with their spectrometer.<sup>1</sup> Precision measurements of the abundances of the isotopes of strontium have been made by Sampson and Bleakney<sup>2</sup> and more recently by Nier<sup>3</sup> with the following results :

Mass number . . . .	84	86	87	88
Abundance (1) . . . .	0·5	9·6	7·5	82·4
(2) . . . .	0·56	9·86	7·02	82·56

(1) Sampson and Bleakney, 1936; (2) Nier, 1938.

The packing fractions of  $^{86}\text{Sr}$  and  $^{87}\text{Sr}$  have been measured by Mattauch<sup>4</sup> by means of natural doublets made by their lines and the lines of silicon trifluoride. The figures obtained, — 9·0 and — 8·7 respectively, are almost certainly too low,<sup>5</sup> but if we assume a more probable value — 7, Nier's abundances give an atomic weight of 87·63 identical with the international chemical value.

*Radiogenic Strontium.* It has long been known that rubidium is radioactive, and that its beta-ray activity should give rise to strontium. Mattauch has demonstrated this transformation very beautifully by means of the mass spectra shown in Plate XI. Hahn, Strassmann and Walling<sup>6</sup> extracted the strontium from mica from Manitoba rich in rubidium but poor in alkaline earths. This material was then analysed by Mattauch with his double focusing mass spectrograph, and the mass spectra in striking contrast to those of ordinary strontium, showed one line only at 87 thus confirming previous conclusions that only one isotope  $^{87}\text{Rb}$  was concerned in the natural radioactivity of that element.

### 39. Yttrium.

The original analysis of the element was made with the first mass spectrograph with an anode containing the fluoride.<sup>7</sup> The spectra showed one line only at 89 which when compared with that of iodine appeared integral within the experimental error. Dempster's recent search<sup>8</sup> has failed to reveal any other isotopes. No determination of the packing fraction has been made, but if we assume a value of about — 7·3 the chemical atomic weight becomes 88·91 in excellent agreement with the international figure 88·92.

<sup>1</sup> *Phys. Rev.*, **49**, 778, 1936.

<sup>2</sup> *Ibid.*, **50**, 456, 1936.

<sup>3</sup> *Ibid.*, **54**, 275, 1938.

<sup>4</sup> *Naturwiss.*, **25**, 170, 1937.

<sup>5</sup> Aston, *Nature*, **143**, 797, 1939.

<sup>6</sup> *Naturwiss.*, **25**, 189, 1937.

<sup>7</sup> Aston, *Phil. Mag.*, **47**, 398, 1924.

<sup>8</sup> *Phys. Rev.*, **55**, 794, 1939.

**40. Zirconium.**

Many abortive attempts were made to obtain the lines of this element and success with the first mass spectrograph was only obtained by the fortunate combination of an exceptionally good setting of the anode-ray discharge tube and a remarkably sensitive schumannized plate.<sup>1</sup> The anode contained a mixture of zirconium fluoride and lithium fluoride, but a considerable quantity of bromine was present from previous experiments. Three of the lines 90, 92, 94, were ascribed with confidence to zirconium. A fourth faint one at 96 was considered doubtful. Rough estimates of abundance agreed with the current chemical atomic weight, and the masses were found integral with bromine to the accuracy of the experiment. No further data were obtained until ten years later,<sup>2</sup> when by the use of wide slits in the second mass spectrograph and more sensitive plates, not only were the four mass numbers above confirmed, but a new one, 91 discovered, which had been overlooked before owing to inferior resolution. Photometry gave the following percentages :

Mass number . . .	90	91	92	94	96
Abundance . . .	48	11.5	22	17	1.5

These give a mean mass number 91.32. If we assume a rough value — 7 for packing fraction and correct for change of scale we get for the atomic weight 91.23 in excellent agreement with the international chemical value 91.22.

**41. Niobium.**

All the early attempts to analyse this element by means of anode rays gave negative results, and success was only attained in 1932 by the use of the volatile pentafluoride.<sup>3</sup> The mass spectra showed one line only 93 with those of its fluorides at 102, 121. It was not possible to measure the packing fraction of niobium with accuracy, but comparison with the line of  $^{28}\text{SiF}_3$  indicated a negative value of about — 8. These results suggested that the chemical atomic weight 93.3, then in use, needed revision. This was done by Honigschmid,<sup>4</sup> who obtained a value  $92.91 \pm 0.01$ . The simplicity of niobium was confirmed later by Sampson and Bleakney.<sup>5</sup> The most probable packing fraction appears now to be about — 6.5. This figure gives an atomic weight identical with the international one 92.91.

<sup>1</sup> Aston, *Nature*, **114**, 273, 1924; *Phil. Mag.*, **49**, 1195, 1925.

<sup>2</sup> *Ibid.*, **133**, 684, 1934; *Proc. Roy. Soc., A*, **149**, 396, 1935.

<sup>3</sup> Aston, *Nature*, **130**, 130, 1932. <sup>4</sup> *Naturwiss.*, **27**, 463, 1934.

<sup>5</sup> *Phys. Rev.*, **50**, 732, 1936.

*42. Molybdenum.*

The first attempts to obtain the mass spectrum of the element were made by the method of accelerated anode rays. These were entirely unsuccessful<sup>1</sup> and the chance of obtaining a suitable volatile compound seemed remote until a specimen of the carbonyl, probably Mo(CO)<sub>6</sub>, was prepared. This is very like the chromium compound in volatility and other physical properties and was found to work almost as satisfactorily when admitted to the discharge bulb in exactly the same way.<sup>2</sup>

The chemical atomic weight of molybdenum is practically a whole number, and Russell, by a theory markedly successful in many cases and founded on analogies from the known radioactive disintegrations, had confidently predicted it to be a simple element of mass number 96.<sup>3</sup> It was, therefore, somewhat surprising to find that its mass spectrum contained no less than seven lines, 92, 94, 95, 96, 97, 98, 100, three of which form isobaric pairs with zirconium. This group shows a similarity of abundance more striking than that of any other element of such complexity.

The total intensity of the group of molybdenum rays was probably less than that yielded by chromium and as this is divided among seven almost equal lines it was by no means easy to get lines dark enough for good photometry even with the maximum practicable exposures. For this reason the group had to be photographed at a position on the plate giving less than the normal resolution. Under these conditions it was only just possible to use the method of intermittent exposures. The small range of intensity rendered a single ratio of 2 to 1 sufficient for the measurements, but the extreme closeness of the lines impairs the accuracy of the photometry so that the ratios were taken as less certain than usual.

A further difficulty was the inevitable presence of the doubly charged mercury group. The very weak line  $^{196}\text{Hg}^{++}$  could be virtually eliminated, but even with the utmost precautions it was not possible to reduce  $^{200}\text{Hg}^{++}$  below a considerable fraction of the practically coincident line  $^{100}\text{Mo}$ . In order to arrive at the true line intensity of the latter the lines of the mercury group had to be photometered up and the effect of the mercury line, estimated from the known ratios of intensity of the mercury group, subtracted. Incidentally these measurements showed that no molybdenum lines of appreciable strength could be present at 99 or 101. On account of these difficulties no great accuracy was claimed for the abundance ratios then obtained which are as given below.

<sup>1</sup> Aston, *Phil. Mag.*, **47**, 399, 1924.

<sup>2</sup> Aston, *Proc. Roy. Soc., A*, **130**, 308, 1931.

<sup>3</sup> Russell, *Nature*, **112**, 588, 1923.

Five years later de Gier and Zeeman<sup>1</sup> analysed the carbonyl by the parabola method, and claimed the discovery of an eighth isotope 102, present to the extent of about 2 to 3 per cent. But recently Mattauch and Lichtblau<sup>2</sup> using the double focusing mass spectrograph and very sensitive Q plates, have obtained excellent mass spectra of molybdenum which show that 102 cannot be present even to one-hundredth the quantity claimed. They estimated the percentage abundances photometrically as given below. Since then the abundances have been estimated electrometrically by Valley,<sup>3</sup> who claims an accuracy of 1 per cent. His figures lie between those of the previous observers as shown.

Mass number . . .	92	94	95	96	97	98	100
Abundance (1) . . .	14.2	10.0	15.5	17.8	9.6	23.0	9.8
(2) . . .	15.5	8.7	16.3	16.8	8.7	25.4	8.6
(3) . . .	14.9	9.40	16.1	16.6	9.65	24.1	9.25

(1) Aston, 1931; (2) Mattauch, 1939; (3) Valley, 1940.

A provisional value for the packing fraction of lines 98 and 100 was obtained by estimating their position among those of mercury. Dempster<sup>4</sup> has compared the packing fractions of the Mo lines with those of Os, Ir and Pt. From his curve that of Mo should be about — 6, a figure supported by the later comparisons of Graves.<sup>5</sup> With Valley's figures for abundance this gives an atomic weight 95.92. The international value is 95.95.

### 43.

This atomic number marks the first gap in the Periodic Table. The element corresponding to it, which should resemble manganese and rhenium in its chemical properties, has not yet been proved to exist naturally, and the original claims for its discovery, made in 1925, have not been substantiated. This is in agreement with general statistical considerations<sup>6</sup> connected with the occurrence of isobars of odd mass number.<sup>7</sup> Quite recently Segré<sup>8</sup> has obtained evidence that it may be formed, of course in infinitesimal quantity, by the bombardment of molybdenum with deuterons or neutrons.

### 44. Ruthenium.

Data for this element were only obtained with difficulty by the use of its volatile tetroxide.<sup>9</sup> The action of this on the discharge was

<sup>1</sup> Proc. Roy. Acad. Amst., 39, 327, 1936.

<sup>2</sup> Zeit. Phys. Chem., 42, 288, 1939.

<sup>3</sup> Phys. Rev., 57, 1058, 1940.

<sup>4</sup> Ibid., 53, 64, 1938.

<sup>5</sup> Ibid., 55, 863, 1939.

<sup>6</sup> Jensen, Naturwiss., 26, 381, 1938.

<sup>7</sup> V. p. 205.

<sup>8</sup> Nature, 143, 460, 1939.

<sup>9</sup> Aston, Proc. Roy. Soc., A, 132, 487, 1931.

even worse than that of the corresponding osmium compound, and the incidental difficulties attending its use so excessive that it must be regarded as lucky that any useful results were obtained at all. Ruthenium appears to have six isotopes with the possibility of a very faint seventh. Only rough estimates of their relative abundance could be made by photometry. They are :

Mass number . . .	96	98	99	100	101	102	104
Abundance . . .	5	?	12	14	22	30	17

Dempster has compared the packing fractions of some of the ruthenium lines with those of platinum and osmium, finding a difference of about 8 in each case.<sup>1</sup> From later work Graves<sup>2</sup> deduces a value  $-5.68 \pm 0.36$  for ruthenium. This will give an atomic weight of 101.1, rather less than the present chemical international value 101.7, but identical with that obtained quite recently by Glen and Rehm.<sup>3</sup>

#### 45. Rhodium.

This element resisted analysis for many years and the first positive results with the second mass spectrograph were very feeble and indicated a single line 103.<sup>4</sup> This result was further confirmed by Dempster.<sup>5</sup> Sampson and Bleakney<sup>6</sup> in a careful search for other isotopes obtained evidence of mass number 101 present to the estimated amount of 1 in 1300, but no others.

Dempster,<sup>7</sup> from measurement of the natural doublet  $^{206}\text{Pb}^{++} - ^{103}\text{Rh}$ , finds a difference of packing fraction of  $7.96 \pm 0.15$ . If we assume a value of about -6 for rhodium the atomic weight is 102.91 identical with the chemical value.

#### 46. Palladium.

One of the last elements to be analysed palladium yielded to Dempster's vacuum spark technique<sup>8</sup> showing six isotopes. The relative abundance of these was measured by Sampson and Bleakney<sup>9</sup> with their mass spectrometer with the following results :

Mass number . . .	102	104	105	106	108	110
Abundance . . .	0.8	9.3	22.6	27.2	26.8	13.5

Dempster<sup>10</sup> has compared the packing fractions of some of the palladium lines with those of lead, thallium and bismuth finding a

<sup>1</sup> *Phys. Rev.*, **53**, 64, 1938.

<sup>2</sup> *Ibid.*, **55**, 863, 1939.

<sup>3</sup> *Zeit. anorg. Chem.*, **235**, 352, 1938.

<sup>4</sup> Aston, *Proc. Roy. Soc., A*, **149**, 396, 1935.

<sup>5</sup> *Nature*, **135**, 993, 1935.

<sup>6</sup> *Phys. Rev.*, **50**, 732, 1936.

<sup>7</sup> *Ibid.*, **53**, 64, 1938.

<sup>8</sup> *Nature*, **136**, 65, 1935.

<sup>9</sup> *Phys. Rev.*, **50**, 732, 1936.

<sup>10</sup> *Ibid.*, **53**, 871, 1938.

difference of almost exactly 8 units in each case.<sup>1</sup> He also measured the position of the line of aluminium amongst those of quadruply charged palladium estimating a difference of  $1\cdot 6 \pm 0\cdot 4$ . These results suggest a mean packing fraction of about — 5 which gives an atomic weight 106.55, a little lower than the international one 106.7.

#### 47. Silver.

This element was first analysed with the first mass spectrograph<sup>2</sup> using rays from an anode containing silver chloride and lithium iodide. Two lines 107 and 109 were observed which appeared integral when compared with the line of iodine. The first of these was slightly the brighter. Owing to the weight of accumulated statistical evidence in connection with the relation between odd atomic number and odd atomic weight,<sup>3</sup> and the exceptional trustworthiness of the work on the chemical atomic weight 107.880, this result might be described as a foregone conclusion. The relative abundance was later<sup>4</sup> measured by photometry and the percentages estimated at 52.5 and 47.5 for 107 and 109 respectively.

Dempster<sup>5</sup> has compared the packing fraction of the silver lines with those of aluminium, iron and zinc. From the first of these relations he estimates the mean packing fraction of the silver lines to be — 4.93 ± 0.5. If we use this value with the abundances given above we get an atomic weight 107.87 in excellent agreement with the chemical value 107.880.

#### 48. Cadmium.

In sharp contrast to zinc and mercury, cadmium is very difficult to deal with in mass-ray analysis. After several failures its lines were first revealed by the first mass spectrograph, using the method of accelerated anode rays.<sup>6</sup> With an anode of cadmium fluoride and lithium fluoride prolonged exposure yielded one mass spectrum showing fairly satisfactory intensity and detail. This was fortunate, for cadmium is so complex an element and its lines so near the limit of resolution that without the enhanced resolving power given by the peculiar properties of schumannized plates it is doubtful if any reliable interpretation could have been made.

Six lines, 110, 111, 112, 113, 114, 116, were identified and their relative abundance roughly estimated. These lines were confirmed by Bainbridge later.<sup>7</sup> In the writer's later investigation with the

<sup>1</sup> V, p. 109.

<sup>2</sup> Aston, *Phil. Mag.*, **47**, 395, 1924.

<sup>3</sup> V, p. 204.

<sup>4</sup> Aston, *Proc. Roy. Soc., A*, **149**, 396, 1935.

<sup>5</sup> *Phys. Rev.*, **53**, 64, 1938.

<sup>6</sup> Aston, *Phil. Mag.*, **49**, 1196, 1925.

<sup>7</sup> *Phys. Rev.*, **43**, 1056, 1933.

second mass spectrograph<sup>1</sup> the volatile methyl was successfully used and much more intense spectra obtained. These showed three more lines 106, 108 and 115 which were all assumed to be isotopes, the relative abundances were also determined by photometry. Bainbridge and Jordan<sup>2</sup> soon after, showed beyond doubt that 115 was due to hydride contamination, and in consequence the figures for abundance were revised<sup>3</sup> as given below. Still more reliable and closely concordant figures were obtained by Nier<sup>4</sup> with his precision mass spectrometer. At the same time he proved the absence of other isotopes to a very high degree. The results for cadmium are :

Mass number . . . .	106	108	110	111	112	113	114	116
Abundance (1) . . . .	1.5	1.0	15.6	15.2	22.0	14.7	24.0	6.0
(2) . . . .	1.4	1.0	12.8	13.0	24.2	12.3	28.0	7.3

(1) Aston, 1935; (2) Nier, 1936.

If we assume a value — 6 for the packing fraction, which has not yet been measured, the atomic weight is 112.37. The chemical value is 112.41.

#### 49. Indium.

In the first successful experiments with this element<sup>5</sup> by anode rays, feeble effects were obtained which showed only one line 115. Later, Wehrli<sup>6</sup> from results with absorption spectra, deduced the presence of mass number 113 and estimated the ratio of abundance as 11 : 1. Indium was later examined with the writer's second mass spectrograph<sup>7</sup> and the presence of 113 confirmed. Its percentage abundance was estimated photometrically as  $4.5 \pm 1$ . This figure was confirmed by Sampson and Bleakney,<sup>8</sup> and the percentages 4.5 and 95.5 adopted in the table for mass numbers 113 and 115. A careful search made by Blewett and Sampson<sup>9</sup> with their mass spectrometer failed to reveal any other isotopes. No data on the packing fraction are available, but if a value — 6 is assumed the atomic weight of indium is 114.81 slightly higher than the international value 114.76.

#### 50. Tin.

This very complex element was first investigated by means of its volatile tetrachloride. The vapour of this compound attacks the tap grease used in the apparatus which makes it difficult to deal with.

<sup>1</sup> Aston, *Proc. Roy. Soc., A*, **149**, 396, 1935.

<sup>2</sup> *Phys. Rev.*, **50**, 282, 1936.

<sup>3</sup> Aston, *Nature*, **137**, 613, 1936.

<sup>4</sup> *Phys. Rev.*, **50**, 1041, 1936.

<sup>5</sup> Aston, *Phil. Mag.*, **49**, 1192, 1925.

<sup>6</sup> *Helv. phys. Acta*, **7**, 611, 1934.

<sup>7</sup> Aston, *Proc. Roy. Soc., A*, **149**, 396, 1935.

<sup>8</sup> *Phys. Rev.*, **50**, 456, 1936.

<sup>9</sup> *Ibid.*, **49**, 778, 1936.

The lines of some of the isotopes of tin were actually visible on one mass spectrum, but could not be identified at the time.<sup>1</sup> The use of the tetramethyl gave much better results and enabled seven isotopes to be identified by the first mass spectrograph.<sup>2</sup>

Xenon happened to be present in the discharge and the appearance of line  $^{120}\text{SnCH}_3$  between  $^{134}\text{Xe}$  and  $^{136}\text{Xe}$  seemed to indicate startling discrepancies between the integral masses of the bodies concerned. When the phenomenon was examined later with the more powerful second mass spectrograph,<sup>3</sup> it was found to be erroneous and probably due to imperfect resolution.<sup>4</sup> No less than eleven lines from 112 to 124 were then observed and ascribed to tin. Their relative intensities were measured by photometry. Later examination of the second order lines of tin by Bainbridge and Jordan<sup>5</sup> showed beyond any doubt that mass number 121 was not present and so on the assumption that hydrides had been present the figures for percentage abundance were corrected<sup>6</sup> as follows :

Mass number	112	114	115	116	117	118	119	120	122	124
Abundance	1.1	0.8	0.4	15.5	9.1	22.5	9.8	28.5	5.5	6.8

The first measurement of the packing fractions was made by examination of the series of lines given by  $\text{SnCH}_3$  molecules and the lines of xenon and shown in Plate VI. The difference in packing fraction between the two elements was estimated to be 2 units. Later these observations were repeated with a more powerful instrument<sup>7</sup> and a provisional value of — 5.8 found for  $^{118}\text{Sn}$  and  $^{120}\text{Sn}$  which, with the latest value for xenon, becomes — 5.5. Graves,<sup>8</sup> by comparison with uranium, deduces the value — 4.56 for three of the isotopes of tin.

### 51. Antimony.

The first experiments on this element made with the hydride  $\text{SbH}_3$  gave negative results which were ascribed to the unstable nature of the compound.<sup>9</sup> Later the vapour of the methyl was used mixed with  $\text{CO}_2$  with success.<sup>10</sup> Its spectrum is characterized by two strong lines 121, 123. Similar pairs appear 15 and 30 units higher in the mass scale due to the mono- and di-methyl molecules respectively. Faint companions at 122 and 124 are safely to be ascribed to hydrides.

By photometry of the antimony lines on spectra obtained later

<sup>1</sup> Aston, *Phil. Mag.*, **42**, 141, 1921. <sup>2</sup> *Ibid.*, **45**, 939, 1923.

<sup>3</sup> Aston, *Proc. Roy. Soc., A*, **115**, 506, 1927. <sup>4</sup> V. p. 89.

<sup>5</sup> *Phys. Rev.*, **50**, 282, 1936. <sup>6</sup> Aston, *Nature*, **137**, 613, 1936.

<sup>7</sup> Aston, *Proc. Roy. Soc., A*, **163**, 391, 1937.

<sup>8</sup> *Phys. Rev.*, **55**, 863, 1939. <sup>9</sup> Aston, *Phil. Mag.*, **42**, 141, 1921.

<sup>10</sup> Aston, *Ibid.*, **45**, 943, 1923.

with the second mass spectrograph<sup>1</sup> the ratio of the abundance of the isotopes 121 and 123 was estimated to be 100 : 78.5, and percentages 56 and 44 have been adopted in the table. No data are available on the packing fraction of antimony, but if we adopt a value — 5.1 intermediate between those of tin and xenon the atomic weight becomes 121.785 in good agreement with the chemical value 121.76.

### 52. Tellurium.

This element is of peculiar interest on account of the anomalous position of its atomic weight with regard to that of iodine in the periodic table. Its properties are not by any means suitable for the production of mass rays and it was in fact the last of the non-metallic elements to be analysed. The early trials with tellurium methyl,<sup>2</sup> and then by volatilizing tellurium or its chloride<sup>3</sup> all failed, but success was achieved to a certain degree by the method of accelerated anode rays when pure tellurium was introduced into the anode.<sup>4</sup> The effects were not strong, but sufficient to identify three isotopes 126, 128, 130. Rough estimates of abundance suggested an atomic weight at least 128.

Later experiments with tellurium chloride, made with the writer's second mass spectrograph, though giving feeble results enabled a new faint isotope 125 to be revealed and the relative abundances to be directly determined by photometry.<sup>5</sup> Line 125 was estimated at 6.6 and 126, 128, 129 at 20.9, 36.1, and 36.4 per cent. respectively. It was also found possible to measure the packing fraction of the lines 126 and 128 by comparing them with  $^{127}\text{I}$ , this may be taken as  $-5 \pm 2$ .

These values were not in good agreement with the accepted chemical atomic weight 127.5, but a little later this discrepancy was removed by the work of Bainbridge<sup>6</sup> who by volatilizing tellurium was able to produce excellent mass spectra such as that shown in Plate VII. These disclosed three additional isotopes 124, 123, 122 and indications of an extremely faint and doubtful one 127. Using the writer's figures, given above, for the stronger lines, to calibrate his plate, Bainbridge worked out the percentages given below. Later Dempster<sup>7</sup> discovered a very weak isotope 120, but no trace of 127. The absence of the latter was also confirmed by Bainbridge and Jordan.<sup>8</sup> The constitution of tellurium is at present taken to be as follows :

Mass number . . .	120	122	123	124	125	126	128	130
Abundance . . .	w	2.9	1.6	4.5	6.0	19.0	32.8	33.1

<sup>1</sup> Aston, *Proc. Roy. Soc.*, A, 132, 492, 1931.

<sup>2</sup> Aston, *Phil. Mag.*, 42, 241, 1921. <sup>3</sup> *Ibid.*, 45, 942, 1923.

<sup>4</sup> *Ibid.*, 49, 1197, 1925. <sup>5</sup> Aston, *Proc. Roy. Soc.*, A, 132, 487, 1931.

<sup>6</sup> Bainbridge, *Phys. Rev.*, 39, 1021, 1932.

<sup>7</sup> *Ibid.*, 50, 186, 1936. <sup>8</sup> *Ibid.*, 50, 282, 1936.

If we assume the most probably packing fraction to be about — 4 the atomic weight becomes 127.59 in good agreement with the international value 127.61.

### 53. Iodine.

The early results with this element<sup>1</sup> were both definite and conclusive. Methyl iodide was used, its vapour being mixed with CO<sub>2</sub> and CH<sub>4</sub>. It gave one strong line at 127 satisfactorily confirmed by another at 142 due to CH<sub>3</sub>I. It was concluded that iodine was a simple element, and this has recently been confirmed by Nier<sup>2</sup> to a very high degree.

An estimate of the packing fraction was made by direct comparison of the single line with that of <sup>128</sup>Xe. No difference between the packing fractions could be observed.<sup>3</sup> From the latest measurements on xenon we may therefore infer a packing fraction of — 4.1 for <sup>127</sup>I. This gives an isotopic weight 126.948 and hence an atomic weight 126.913. The present international one is 126.92 and the latest chemical determination<sup>4</sup> gives 126.915.

### 54. Xenon.

The first mass spectrum of xenon indicated five isotopes, but it was feeble and indistinct and their mass numbers were estimated a unit too low.<sup>5</sup> Soon after by the use of a richer specimen of heavy inert gases these figures were corrected and two more isotopes 128, 131 indicated. During the critical examination of the heavier constituents of air for element 86 faint effects were seen at 124, 126. These were later confirmed on the second mass spectrograph during investigations on its packing fraction.<sup>6</sup> All nine isotopes of xenon will be seen in Plate VI.

The relative abundance of the isotopes of xenon were first measured by photometry.<sup>7</sup> As the lines were too close together to use the method of intermittent exposures a large number of spectra were taken with different exposures and from them a curve such as that in Fig. 24 constructed. The results are given below. Seven years later more accurate spectrometer values were obtained by Nier<sup>8</sup> who also

<sup>1</sup> Aston, *Phil. Mag.*, **42**, 141, 1921.

<sup>2</sup> *Phys. Rev.*, **52**, 933, 1937.

<sup>3</sup> Aston, *Proc. Roy. Soc., A*, **115**, 487, 1927.

<sup>4</sup> Baxter and Lundstedt, *J. Amer. Chem. Soc.*, **62**, 1829, 1940.

<sup>5</sup> Aston, *Phil. Mag.*, **39**, 623, 1920.

<sup>6</sup> Aston, *Proc. Roy. Soc., A*, **115**, 487, 1927.

<sup>7</sup> Aston, *Ibid., A*, **126**, 511, 1930.

<sup>8</sup> *Phys. Rev.*, **52**, 933, 1937.

showed the absence of other mass numbers to a very high degree. Percentages derived from his results are :

Mass number . .	124	126	128	129	130	131	132	134	136
Abundance (1) . .	0.08	0.08	2.30	27.13	4.18	20.67	26.45	10.31	8.79
(2) . .	0.094	0.088	1.90	26.23	4.07	21.17	26.96	10.54	8.95

(1) Aston, 1930 ; (2) Nier, 1937.

Nier considers his abundances to be correct to 1 per cent., except for 126 and 124 which are correct to 3 per cent. These figures do not support the conclusion of de Gier and Zeeman <sup>1</sup> that <sup>126</sup>Xe is about half as strong as <sup>124</sup>Xe. An explanation of this has been suggested on p. 90.

Xenon was one of the elements examined by the writer in his first survey of packing fractions <sup>2</sup> owing to the fact that its line 134 could be photographed in the second order between two third order lines of mercury, without its position being seriously disturbed by the weak mercury isotope 201. In this way a provisional value of — 5.3 was deduced. Much more reliable values have recently been obtained <sup>3</sup> by measurements of the doublets of third order xenon and hydrocarbons shown in Plate VIII, with results tabulated on p. 105. Correcting for the later values of carbon and hydrogen the mean packing fraction of xenon can be taken as about — 4.1. With Nier's abundances this gives an atomic weight 131.30, identical with the international value deduced from density determinations.

### 55. Cæsium.

When this element was first investigated <sup>4</sup> by a heated anode of cæsium chloride, only one line appeared, corresponding to mass number 133, although the chemical atomic weight was then 132.81. The simplicity of cæsium was confirmed later to a high degree by Bainbridge <sup>5</sup> who used as a source of its rays a tantalum strip coated with pollucite. He quotes the percentages of hypothetical lighter components required to bring its atomic weight into agreement with the chemical value, and states : "No indication has been obtained of any single one of the possible isotopes being present to even one-tenth of the above percentages."

As the only other obvious explanation of the low chemical weight would be an abnormal packing fraction of — 14.3 this quantity was measured directly by means of a special discharge tube by which the

<sup>1</sup> Proc. Roy. Acad. Amst., 39, 329, 1936.

<sup>2</sup> Aston, Proc. Roy. Soc., A, 115, 487, 1927.

<sup>3</sup> Aston, Ibid., A, 163, 391, 1937.

<sup>4</sup> Aston, Phil. Mag., 42, 436, 1921.

<sup>5</sup> Bainbridge, Phys. Rev., 36, 1668, 1930.

cæsium line could be photographed between the lines 132 and 134 of xenon of which the packing fraction is known. No abnormality was found and the most probable packing fraction of cæsium was given as  $-5 \pm 2$ ,<sup>1</sup> which indicated an atomic weight 132.917. The discrepancy has since been removed by a revision of the chemical atomic weight.

Nier<sup>2</sup> pushed the search for other possible isotopes even further than Bainbridge without success, so that cæsium may be regarded as being simple to a very high degree. If we assume a packing fraction  $-4.1$ , the value recently obtained for xenon, the isotopic weight of  $^{133}\text{Cs}$  becomes 132.9455, and the atomic weight of the element 132.909, in excellent agreement with the present international chemical one 132.91.

### 56. Barium.

The early results obtained from barium by accelerated anode rays using an anode of barium chloride and lithium bromide were misleading, only one line 138 being detected.<sup>3</sup> The explanation of this became clear when, by the use of the high resolving power of the second mass spectrograph and very long exposures three more isotopes 135, 136, 137 were discovered.<sup>4</sup> These lines are faint and in ascending order of intensity so that with the imperfect resolution of the original instrument they were quite indistinguishable from a naturally graded penumbra of the much more intense line 138. The relative abundances of the isotopes were measured photometrically giving the figures adopted in the first table of isotopes and quoted below.

A determination of the packing fraction of  $^{138}\text{Ba}$  was made by means of the special arrangement of the discharge tube described for cæsium. The anode contained  $\text{BaCl}_2$  and  $\text{LiI}$  and the comparison line used was that at 139 due to IC, which together with ICH and ICH<sub>2</sub> appeared strongly under these conditions. The resulting figure was  $-6.1 \pm 2$ . From this the atomic weight of barium worked out on the chemical scale to be 137.43 in reasonable agreement with the accepted chemical value 137.36.<sup>5</sup>

Four years later Blewett and Sampson, using barium oxide on a tungsten filament,<sup>6</sup> discovered a fifth isotope 134 which they estimated at 1.8 per cent. Dempster<sup>7</sup> confirmed this isotope and discovered two rarer ones 130 and 132 (*v. Plate IX*). These were confirmed by Sampson and Bleakney<sup>8</sup> who redetermined the abundance ratios with

<sup>1</sup> Aston, *Proc. Roy. Soc., A*, **134**, 573, 1932.

<sup>2</sup> *Phys. Rev.*, **52**, 933, 1937. <sup>3</sup> Aston, *Phil. Mag.*, **49**, 1192, 1925.

<sup>4</sup> Aston, *Proc. Roy. Soc., A*, **134**, 576, 1932.

<sup>5</sup> Aston, *Ibid.*, **576**, 1932.

<sup>7</sup> *Ibid.*, **947**, 1936.

<sup>6</sup> *Phys. Rev.*, **49**, 778, 1936.

<sup>8</sup> *Ibid.*, **50**, 456, 1936.

results given below. Still more recently Nier,<sup>1</sup> using as a source the vapour of the pure metal, obtained the following abundances, finding much more 132 than did Sampson and Bleakney. Nier also proved the absence of other isotopes to a very high degree. The results for Barium are :

Mass number .	. 130	132	134	135	136	137	138
Abundance (1)	. —	—	—	5·9	8·9	11·1	74·1
(2)	. 0·16	0·015	1·72	5·7	8·5	10·8	73·1
(3)	. 0·101	0·097	2·42	6·6	7·8	11·3	71·7

(1) Aston, 1932 ; (2) Sampson and Bleakney, 1936 ; (3) Nier, 1938.

The most probable packing fraction from modern data is about — 4. This gives an atomic weight 137·33 in good agreement with the international one 137·36.

### 57. Lanthanum.

This element was investigated by means of its bromide, which when mixed with lithium bromide, worked smoothly as an anode.<sup>2</sup> With an exposure of half an hour a single line 139 was obtained of such a strength as to make it reasonably certain that lanthanum was a simple element, as the chemical atomic weight 138·90, then in use, led one to expect. Quite recently the packing fraction of <sup>139</sup>La has been estimated by Dempster<sup>3</sup> from the position of its triply charged line between the lines of titanium 46 and 47. Assuming values for the latter identical with <sup>48</sup>Ti, that is — 7·2, the packing fraction of <sup>139</sup>La is — 3·2. This gives an atomic weight 138·92 identical with the international chemical value now in use.

### 58. Cerium.

Early results from cerium were obtained by anode rays from its bromide.<sup>4</sup> These showed a strong line 140 and a weak one 142. Examination with the second mass spectrograph<sup>5</sup> confirmed these mass numbers and by photometry the abundance of the heavier was estimated at 11 per cent. Later Dempster<sup>6</sup> identified two very faint components 136 and 138, but gave no estimate of their abundance. If we regard them as negligible and use a packing fraction of — 3 an atomic weight 140·14 is obtained in excellent agreement with the chemical value 140·13.

<sup>1</sup> *Phys. Rev.*, 54, 275, 1938.

<sup>2</sup> Aston, *Phil. Mag.*, 49, 1191, 1925.

<sup>3</sup> *Phys. Rev.*, 53, 869, 1938.

<sup>4</sup> Aston, *Phil. Mag.*, 49, 1191, 1925.

<sup>5</sup> Aston, *Proc. Roy. Soc., A*, 146, 46, 1934.

<sup>6</sup> *Phys. Rev.*, 49, 947, 1936.

### 59. *Praseodymium.*

In the original analysis using an anode containing the pure bromide <sup>1</sup> a single line 141 was obtained. This evidence and the chemical atomic weight 140.92 made it reasonably certain that praseodymium was a simple element of mass number 141. No further work has been reported. Assuming a packing fraction of — 3 the atomic weight is 140.91 in good agreement with the international value 140.92.

### 60. *Neodymium.*

The first analysis by anode rays from the bromide was obtained with great difficulty. Mass numbers 142, 144, 146 were identified with 145 doubtful.<sup>2</sup> In the later survey <sup>3</sup> these four were confirmed, a fifth, 143 was discovered and the relative abundances roughly estimated by photometry. The atomic weight deduced was substantially lower than that obtained by chemical methods and when lines 148 and 150 were obtained by Dempster <sup>4</sup> from a mixture of rare earth containing neodymium, it was pointed out that the presence of these isotopes might remove the discrepancy.<sup>5</sup> These lines were confirmed as true isotopes by Dempster <sup>6</sup> and more accurate photometric measurements of abundance have been made by Mattauch and Hauk <sup>7</sup> which have been adopted in the table. These are :

Mass number . . . . .	142	143	144	145	146	148	150
Abundance . . . . .	25.95	13.0	27.6	9.2	16.5	6.8	5.95

The packing fractions of some of the isotopes of neodymium have been estimated by Dempster <sup>8</sup> by comparing their third order lines with the first order lines of titanium. On the assumption that the isotopes of titanium all had identical values — 7.2, he deduces — 2.6, — 2.41 and — 2.6 for the isotopes 146, 148 and 150 of neodymium respectively. If we apply these values to the mean mass number 144.404 given by Mattauch and Hauk the atomic weight of neodymium is 144.33. The international chemical value is 144.27.

### 61.

This atomic number marks the second gap in the Periodic Table. The chemical properties of such an element can be inferred to be those of a rare earth. It has been searched for in the past with the

<sup>1</sup> Aston, *Phil. Mag.*, **49**, 1191, 1925.

<sup>2</sup> Aston, *Ibid.*

<sup>3</sup> Aston, *Nature*, **132**, 930, 1933; *Proc. Roy. Soc., A*, **146**, 46, 1934.

<sup>4</sup> *Proc. Amer. Phil. Soc.*, **75**, 735, 1935.

<sup>5</sup> Aston, *Nature*, **137**, 613, 1936.

<sup>6</sup> *Phys. Rev.*, **51**, 589, 1937.

<sup>7</sup> *Naturwiss.*, **25**, 780, 1937.

<sup>8</sup> *Phys. Rev.*, **53**, 869, 1938.

utmost diligence, but so far none of the claims to its discovery in nature have been substantiated. From general statistical considerations it is probably unstable.<sup>1</sup>

### 62. Samarium.

This element was analysed by means of the second mass spectrograph using anode rays as a source.<sup>2</sup> Four strong lines and two weak ones were observed and their abundances estimated by photometry as follows :

Mass number . . .	144	147	148	149	150	152	154
Abundance . . .	3	17	14	15	5	26	20

These approximate values correspond to a mean mass number  $150.2 \pm 0.2$ . The atomic weight will be 150.13 rather lower than the international value 150.43 but the difference has little significance owing to the uncertainty of the abundances.

### 63. Europium.

The mass spectrum of this element, first analysed by anode rays<sup>3</sup> showed twin lines 151 and 153 of nearly equal intensity. Photometry indicated that the lighter was slightly the more abundant, the percentages being estimated at 50.6 and 49.4 respectively. Quite recently the analysis has been repeated with a double focus mass spectrograph and more sensitive plates by Lichtblau<sup>4</sup> who finds the heavier isotope the more abundant in the ratio  $100 : 96.3 \pm 1.2$ . From this he deduces an atomic weight  $151.95 \pm 0.01$ . The international one is 152.0.

### 64. Gadolinium.

In the first analysis by anode rays<sup>5</sup> five isotopes 155, 156, 157, 158 and 160 were observed, and their relative abundances estimated as given below. This result indicated that the chemical atomic weight then in use, 157.3, was too high. A revision was made by Naeser and Hopkins<sup>6</sup> who obtained  $156.85 \pm 0.011$ . An international value 156.9 was adopted in 1936. Later Pool and Quill<sup>7</sup> from observations on the radioactivity induced in gadolinium by neutrons, deduced that a stable 152 should exist, and a search by Dempster<sup>8</sup> revealed small

<sup>1</sup> Jensen, *Naturwiss.*, **26**, 381, 1938.

<sup>2</sup> Aston, *Nature*, **132**, 930, 1933; *Proc. Roy. Soc., A*, **146**, 46, 1934.

<sup>3</sup> *Ibid.*

<sup>4</sup> *Naturwiss.*, **27**, 260, 1939.

<sup>5</sup> Aston, *Nature*, **132**, 930, 1933; *Proc. Roy. Soc., A*, **146**, 46, 1934.

<sup>6</sup> *J. Amer. Chem. Soc.*, **57**, 2183, 1935.

<sup>7</sup> *Phys. Rev.*, **53**, 437, 1938.

<sup>8</sup> *Ibid.*, 727, 1938.

## 66. DYSPROSIUM

percentages of 152 and 154. The values adopted for gadolinium are :

Mass number . . .	152	154	155	156	157	158	160
Abundance . . .	0·2	1·5	21	22	17	22	16

The only measurement of the packing fraction of gadolinium has been made recently by Graves<sup>1</sup> using Dempster's hot spark method. He compared the positions of its lines with those of chromium getting a mean difference of packing fraction of 6·37. If we take the latest value of chromium — 8·0 that of gadolinium will be — 1·6. This when combined with abundances given above gives an atomic weight 156·93 in good agreement with the international value 156·9.

## 65. Terbium.

In the first analysis anode rays from terbium bromide showed one line of satisfactory intensity at 159.<sup>2</sup> This result did not accord with the chemical value of the atomic weight 159·2, then in use. A revision was made by Marsh<sup>3</sup> who obtained a value 158·89 in good agreement with the mass spectrum result. This work was discussed by the International Atomic Weights committee in their report for 1936,<sup>4</sup> but the new figure was not adopted. If we assume a probable packing fraction of — 1 the atomic weight is 158·94 suggesting that the present international value 159·2 is considerably too high.

## 66. Dysprosium.

Results with this element were only obtained with considerable difficulty by means of anode rays from its bromide.<sup>5</sup> They showed four isotopes 161, 162, 163, 164 of nearly equal abundance as shown below. Later Pool and Quill<sup>6</sup> predicted a stable 160 and this was found, together with a still rarer 158 by Dempster,<sup>7</sup> who estimated their abundance at 1·5 and 0·1 per cent. respectively. These results show the constitution of dysprosium to be :

Mass number . . .	158	160	161	162	163	164
Abundance . . .	0·1	1·5	22	24	24	28

These figures correspond to a mean mass number 162·55 and with a probably packing fraction of — 1 give an atomic weight 162·49 in good agreement with the international value 162·46.

<sup>1</sup> *Phys. Rev.*, 55, 865, 1939.

<sup>2</sup> Aston, *Nature*, 132, 930, 1933; *Proc. Roy. Soc., A*, 146, 46, 1934.

<sup>3</sup> *J. Chem. Soc.*, 772, 1935.

<sup>4</sup> *J. Amer. Chem. Soc.*, 58, 541, 1936.

<sup>5</sup> Aston, *Nature*, 133, 327; *Proc. Roy. Soc., A.*, 146, 46, 1934.

<sup>6</sup> *Phys. Rev.*, 53, 437, 1938. <sup>7</sup> *Ibid.*, 727, 1938.

**67. Holmium.**

This element analysed by anode rays from its bromide gave very satisfactory results showing it to be simple, of mass number 165.<sup>1</sup> Adopting — 1·3 as the most probable packing fraction the atomic weight is 164·934. The international value was 163·5, but the latest figure 164·94, adopted in the 1941 Report, from the work of Honigschmid<sup>2</sup> is in excellent agreement with the mass spectrum results.

**68. Erbium.**

This element has peculiar interest in respect to its atomic weight deduced chemically and that indicated by its mass spectrum. Faint results from an impure sample of erbium bromide had been obtained as early as 1924 with the writer's first mass spectrograph<sup>3</sup> and when the analysis of anode rays from its bromide was undertaken with his second,<sup>4</sup> ten years later, particular care was taken to obtain the purest material possible for the purpose. This was a sample of the material used just previously by Honigschmid for an atomic weight determination which had resulted in an unexpectedly low value 165·204.<sup>5</sup> The current international figure was 167·64. The mass spectrum showed four lines only, 166, 167, 168, 170, and their percentage abundance, measured photometrically, and given below, indicated a mean mass number 167·24, so that, even allowing for possible less abundant lighter constituents, Honigschmid's low value appeared completely untenable. A later examination of the material showed that it contained an entirely unexpected percentage of the light element yttrium, which had been previously overlooked in the X-ray analysis, and a new value 167·24 was obtained by Honigschmid and Wittner.<sup>6</sup>

Recently Pool and Quill<sup>7</sup> predicted a stable isotope 164, which together with a still rarer one, 162, was discovered by Dempster.<sup>8</sup> The figures for erbium are :

Mass number .	162	164	166	167	168	170
Abundance . .	0·25	2	35	24	29	10

With a probable packing fraction nearly zero these correspond to an atomic weight 167·12. The international value is 167·2, but as no great accuracy is claimed for the relative abundance of the main isotopes this discrepancy is not significant.

<sup>1</sup> Aston, *Nature*, **133**, 327, 1934; *Proc. Roy. Soc., A*, **146**, 46, 1934.

<sup>2</sup> *Naturwiss.*, **27**, 855, 1939. <sup>3</sup> Aston, *Nature*, **113**, 856, 1924.

<sup>4</sup> Aston, *ibid.*, **133**, 327; *Proc. Roy. Soc., A*, **146**, 46, 1934.

<sup>5</sup> *Zeit. Anorg. Chem.*, **214**, 97, 1933.

<sup>6</sup> *Naturwiss.*, **24**, 619, 1936; *Zeit. Anorg. Chem.*, **233**, 113, 1937.

<sup>7</sup> *Phys. Rev.*, **53**, 437, 1938. <sup>8</sup> *Ibid.*, 727, 1938.

### 69. *Thulium.*

Analysis of the anode rays from the bromide by the second mass spectrograph<sup>1</sup> showed a single line 169. No trace of any other could be seen and thulium appears to be simple. With the most probable packing fraction the atomic weight is 168·93, so the present international chemical value, 169·4, is probably too high.

### 70. *Ytterbium.*

Analysed by the second mass spectrograph using anode rays from its bromide<sup>2</sup> five lines were observed and their relative abundance estimated roughly by photometry as given below. Later Pool and Quill<sup>3</sup> predicted a stable 170. This and a still rarer 168 were discovered by Dempster.<sup>4</sup> The figures for ytterbium are :

Mass number . . .	168	170	171	172	173	174	176
Abundance . . .	0·06	2	9	23	17	37	12

These give an atomic weight of  $173\cdot2 \pm 0\cdot2$ . The international value is 173·04. The recent work of Schuler and Roig<sup>5</sup> suggests that the ratio of abundance of 173 to 171 is 1·14, considerably less than that given by the photometry of the mass spectra.

### 71. *Lutecium.*

In the writer's experiments with his second mass spectrograph<sup>6</sup>, anode rays from the bromide showed one line only, 175. It was assumed that lutecium was simple and its atomic weight estimated as  $174\cdot91 \pm 0\cdot05$ . Later Gollnow,<sup>7</sup> from hyperfine structure, predicted a second constituent, either 173 or 177, present to the extent of 1·5 per cent. A revision of the chemical atomic weight by Honigschmid<sup>8</sup> gave a value 174·98, which was taken as indicating the presence of 177, but Dempster<sup>9</sup> searching for this mass number failed to detect it. The matter has now been cleared up in a somewhat unexpected and dramatic manner by the work of Mattauch and Lichtblau,<sup>10</sup> who by means of the mass spectrograph have identified the heavier isotope to be 176, present to the extent of 2·5 per cent. This gives a mean mass number 175·025, and if we take the most

<sup>1</sup> Aston, *Nature*, **133**, 327, 1934; *Proc. Roy. Soc., A*, **146**, 46, 1934.

<sup>2</sup> *Ibid.*

<sup>3</sup> *Phys. Rev.*, **53**, 437, 1938.

<sup>4</sup> *Ibid.*, 727, 1938.

<sup>5</sup> *Zeit. Physik*, **111**, 165, 1938.

<sup>6</sup> Aston, *Nature*, **133**, 327; *Proc. Roy. Soc., A*, **146**, 46, 1934.

<sup>7</sup> *Zeit. Physik*, **103**, 443, 1936. <sup>8</sup> *Naturwiss.*, **25**, 748, 1937.

<sup>9</sup> *Phys. Rev.*, **55**, 794, 1939.

<sup>10</sup> *Zeit. Phys.*, **111**, 514, 1939.

probable packing fraction as zero, the atomic weight is 174.99. This value is identical with the latest determination made by Honigschmid<sup>1</sup> and is in good agreement with the international figure 175.0.

### 72. *Hafnium.*

Many attempts were made to obtain results from this newly discovered element but without success until, using the technique found successful with the rare earths, anode rays were produced from the fluoride.<sup>2</sup> These indicated five mass numbers, 176, 177, 178, 179, 180, and the relative abundance was roughly estimated by photometry as given below. A later search by Dempster<sup>3</sup> has revealed a rare isotope, 174, estimated at 0.3 per cent., and possibilities of another, 172, which he regards as doubtful. The figures for hafnium are :

Mass number . . .	172	174	176	177	178	179	180
Abundance . . .	?	0.3	5	19	28	18	30

Assuming the packing fraction to be positive and about 1 the atomic weight is  $178.5 \pm 0.2$ , in good agreement with the international value 178.6.

### 73. *Tantalum.*

This element resisted all attempts until it was analysed by means of its pentafluoride at the same time as niobium.<sup>4</sup> Like the latter, it proved to be simple, giving a single line at 181 followed by 200, 219 . . . due to TaF, TaF<sub>2</sub>, . . . Neither the line at 183, expected from its atomic weight, nor any other could be detected even to one-fiftieth the intensity of the main line. Its packing fraction was estimated to be — 4 from the position of line 200 in the mercury group. This result made it clear that the international atomic weight 181.4, then in use, was too high. A revision of this was made and the value 180.88 obtained by Honigschmid and Schlee.<sup>5</sup> A recent search by Dempster<sup>6</sup> has confirmed the simplicity of tantalum to a high degree. No further measurements of the packing fraction have been recorded, and the first estimate would now become — 3 with the later value for mercury. This figure is probably too low but gives an atomic weight virtually identical with the international one, 180.88.

<sup>1</sup> *Zeit. Anorg. Chem.*, **240**, 284, 288, 1939.

<sup>2</sup> Aston, *Nature*, **133**, 684, 1934; *Proc. Roy. Soc., A*, **149**, 396, 1935.

<sup>3</sup> *Phys. Rev.*, **55**, 794, 1939.

<sup>4</sup> Aston, *Nature*, **130**, 130, 1932.

<sup>5</sup> *Zeit. Anorg. Chem.*, **221**, 129, 1934; **225**, 64, 1935.

<sup>6</sup> *Phys. Rev.*, **55**, 794, 1939.

**74. Tungsten.**

An attempt to obtain the mass spectrum of this element by means of its volatile hexafluoride was unsuccessful,<sup>1</sup> but good results were obtained later with the second mass spectrograph by the use of its hexacarbonyl.<sup>2</sup> The procedure adopted was the same as that with the corresponding compound of molybdenum, but owing to its smaller volatility and the greater atomic weight of tungsten the effects were much weaker and it was only by long exposures and the use of Q plates that lines of satisfactory intensity were obtained.

Four mass numbers, 182, 183, 184 and 186, were observed. In order to measure the relative abundance of the isotopes of tungsten it was assumed that their photographic effect would be the same as that of the slightly heavier ones of mercury. The lines of the latter were, therefore, photographed on the same plate with a graduated series of suitably short exposures, and from the known abundances of the mercury isotopes those of tungsten were deduced. Recently Dempster<sup>3</sup> discovered an additional very rare isotope, 180, estimated to be about 1 per cent. as abundant as 183. Making allowance for this in the original figures we get :

Mass number . . .	180	182	183	184	186
Abundance . . .	0.2	22.6	17.3	30.1	29.8

The packing fraction of tungsten was originally estimated to be indistinguishable from that of mercury<sup>4</sup> of which the latest value is 1.7. Dempster<sup>5</sup> has measured its doubly charged lines against those of zirconium and finds a difference of about 8 units. He gives the packing fraction of tungsten on his curve<sup>6</sup> as a little less than 2. If we assume a value 1.7 the atomic weight is 183.94, in excellent agreement with the international value 183.92.

**75. Rhenium.**

This recently discovered element was investigated by means of its volatile heptoxide.<sup>7</sup> The way in which its analysis was accomplished is an excellent illustration of the capricious nature of the problem of producing mass rays by means of the discharge tube. The substance, which is a highly hygroscopic crystalline solid, was first treated in the same way as osmium tetroxide, but although a somewhat similar disturbance of the discharge made it clear that doses of the vapour had entered the bulb, yet no rhenium lines were obtained. The solid was

<sup>1</sup> Aston, *Proc. Roy. Soc., A*, **115**, 507, 1927.

<sup>2</sup> *Ibid.*, **A**, **132**, 491, 1931. <sup>3</sup> *Phys. Rev.*, **52**, 1074, 1937.

<sup>4</sup> Aston, *Proc. Roy. Soc., A*, **132**, 491, 1931. <sup>5</sup> *Phys. Rev.*, **53**, 64, 1938.

<sup>6</sup> *Ibid.*, 869, 1938. <sup>7</sup> Aston, *Proc. Roy. Soc., A*, **132**, 496, 1931.

then introduced into the bulb itself, as had been selenium and tellurium tetrachloride, but notwithstanding the fact that the distillation was made so copious that a visible layer was formed on the glass walls, still no lines could be seen. At this stage work on the element was abandoned as quite hopeless and preparations were made to proceed to the next. By a piece of remarkable good fortune this happened to be gold which it was intended to attack by means of its slightly volatile chloride. This compound gives off chlorine when heated and as previously it had been noticed that the presence of a halogen gas often stimulated the appearance of lines otherwise faint, it was considered just worth while to make one trial with it *before* the rhenium oxide deposit had been removed from the walls. This procedure was successful beyond all hopes. Although no lines of gold were visible the rhenium doublet appeared in great strength and was repeated 16, 32 and 48 units higher as  $\text{ReO}$ ,  $\text{ReO}_2$  and  $\text{ReO}_3$ , in this way providing unusually convincing evidence of its isotopic constitution.

The fact that it consists of isotopes 185 and 187 was expected from the general rule that complex elements of odd atomic number (above 9) consist of two odd mass numbers two units apart, but it is of interest as being the first odd element analysed in which the heavier constituent is the more abundant. The ratio of this abundance was established photometrically, by analogy with the mercury lines, to be 1·62. The favourable position of line 203 due to  $^{187}\text{ReO}$  among those of mercury enabled an estimate of its packing fraction to be obtained with comparative ease. Correcting for the latest value for mercury this becomes zero, giving for the atomic weight  $186\cdot18 \pm 0\cdot07$ . The international value is 186·31.

### 76. Osmium.

This element was investigated by means of its tetroxide.<sup>1</sup> This is a solid sufficiently volatile for use, but the effect of introducing its vapour into the normal discharge is quite amazing. The best analogy is that of the injection of a violent drug, such as strychnine, into a living organism. The ordinary mechanism of the discharge appears to be completely upset and only slowly recovers. No doubt part of this transformation is due to the decomposition of the compound in the body of the discharge, but in addition the vapour appears to act on the surface of the wax forming the joint between the bulb and the mass spectrograph, depositing a layer, presumably of osmium, which while fresh behaves somewhat like a Wehnelt cathode. The best way of minimizing these objectionable properties was to admit small doses intermittently while the discharge was being fed with a

<sup>1</sup> Aston, *Proc. Roy. Soc., A*, 132, 487, 1931.

small leak of CO<sub>2</sub>. Six isotopes, 186, 187, 188, 189, 190, 192, were observed and their relative abundance estimated by photometry as shown below. These mass numbers were confirmed and a seventh rare one, 184, discovered by Nier<sup>1</sup> who redetermined the abundances by his much more accurate electric method with the following results.

Mass number . .	184	186	187	188	189	190	192
Abundance (1) . —		1·0	0·6	13·4	17·4	25·1	42·5
(2) . 0·018	1·58	1·64	13·3	16·2	26·4	40·9	

(1) Aston, 1931; (2) Nier, 1937.

The 1931 figures with the data then available indicated an atomic weight 190·31, as against the international value then in use of 190·8. In spite of this a still higher value, 191·5, was adopted in 1934 from chemical evidence.

A value of the packing fraction of osmium, rough but accurate enough for fixing the atomic weight, was obtained in 1931 from the relative positions of its lines and those of mercury. A figure of 2·0 has lately been deduced by Graves.<sup>2</sup> With this and Nier's abundances the atomic weight becomes 190·26. The international value 190·2, adopted for 1939, depends purely on mass spectrum evidence.

### 77. Iridium.

This was the last stable element to yield to mass spectrum analysis. If it followed the rule associated with the heavier elements of odd atomic number<sup>3</sup> and its chemical atomic weight 193·1 was trustworthy, it should consist of mass numbers 193 and 195, the lighter predominating. Venkatasachar and Sibaiya<sup>4</sup> from the hyperfine structure of iridium lines showed that two isotopes were present, the heavier predominating in the ratio of about 2 to 1. Since mass number 195 had been already shown to be present in considerable abundance in platinum, and isobars of odd mass number are extremely rare,<sup>5</sup> they assigned 191 and 193 to iridium and concluded that the atomic weight was too high. This conclusion was verified a little later by Dempster<sup>6</sup> who by sparks from a platinum iridium alloy obtained a mass spectrum showing the lines 191 and 193, the heavier being the more abundant, as in the cases of rhenium and thallium. Sampson and Bleakney,<sup>7</sup> using the ionized metallic vapour in their mass spectrometer found the relative abundance of 191 and 193 to be 38·5 and 61·5 per cent. respectively.

Dempster<sup>8</sup> has compared the doubly charged lines of iridium with

<sup>1</sup> *Phys. Rev.*, 52, 885, 1937.

<sup>2</sup> *Ibid.*, 55, 863, 1939.

<sup>3</sup> V. p. 204.

<sup>4</sup> *Nature*, 136, 437, 1935.

<sup>5</sup> V. p. 205.

<sup>6</sup> *Nature*, 136, 909, 1935.

<sup>7</sup> *Phys. Rev.*, 50, 732, 1936.

<sup>8</sup> *Ibid.*, 53, 64; 869, 1938.

singly charged molybdenum and shown a difference of packing fraction of a little less than 8 units. From his curve the packing fraction of iridium would be about 2. If we use this figure the atomic weight of iridium is 192.22, indicating that the international chemical one, 193.1, is too high.

### 78. Platinum.

Many attempts to analyse this element by anode rays or the use of its volatile compounds all failed, and it was only in 1935 that Dempster,<sup>1</sup> by his vacuum spark method, obtained its five lines, 192, 194, 195, 196, 198, of which he remarks, "the middle three form a triplet of almost equal strength, while the heaviest is decidedly weaker and the lightest very faint." Independently Fuchs and Kopfermann<sup>2</sup> and Venkatasachar<sup>3</sup> deduced the complexity of platinum by observations on its hyperfine structure, and in later work on this several estimates of the relative abundance of its isotopes were made.<sup>4</sup> These show considerable variation, and more satisfactory figures, given below, were obtained by Sampson and Bleakney<sup>5</sup> with their permanent magnet mass spectrometer.

Mass number	192	194	195	196	198
Abundance	0.8	30.2	35.3	26.6	7.2

The packing fraction of platinum has been measured by Dempster<sup>6</sup> by comparing its triply charged lines with those of copper. He gives it as  $2.03 \pm 0.3$  which makes the atomic weight 195.14, slightly lower than the international one, 195.23.

### 79. Gold.

From statistical considerations, and the fact that its chemical atomic weight seemed well established as 197.2, gold was early predicted to consist of two isotopes 197 and 199, the lighter being, as is usual, the more abundant. Its possible isotopic constitution rose to some importance in 1924 owing to claims, now abandoned, that it could be made from mercury by transmutation, but all attempts to obtain its mass spectrum failed. One of them is described on page 179. It was not till 1935 that Dempster, by his vacuum spark method,<sup>7</sup>

<sup>1</sup> *Nature*, **135**, 993, 1935.

<sup>2</sup> *Naturwiss.*, **23**, 372, 1935.

<sup>3</sup> *Proc. Ind. Acad. Sci.*, A, **1**, 955, 1935.

<sup>4</sup> Venkatasachar and Sibaia, *ibid.*, **2**, 101, 1935; Jaeckel and Kopfermann, *Zeit. Phys.*, **99**, 492, 1936; Tolansky and Lee, *Nature*, **137**, 908, 1936; Kopfermann and Krebs, *Zeit. Phys.*, **101**, 193, 1936.

<sup>5</sup> *Phys. Rev.*, **50**, 732, 1936.

<sup>6</sup> *Ibid.*, **53**, 64, 1938.

<sup>7</sup> *Nature*, **136**, 65, 1935.

obtained from it a single line, 197. Although line 199 was carefully searched for it was not present to an appreciable extent, a result confirmed by Imanishi<sup>1</sup> from observations on band spectra. Gold is evidently simple to a high degree.

Its packing fraction has been estimated as  $2.0 \pm 0.4$  by Dempster.<sup>2</sup> This gives an atomic weight 196.98. It seems certain that the international chemical value 197.2 is too high.

### *80. Mercury.*

This element has a unique position of importance in the technique of mass spectra. As it is usually employed in the exhaustion and admission of gas in the apparatus for the ordinary discharge, and is particularly favourable to the production of mass rays it is extremely difficult to eliminate it from mass spectra obtained in this way. This is fortunately neither necessary nor desirable in most cases, for it provides a valuable reference scale and, for some reason unknown, its presence is definitely beneficial to the smooth running of the discharge tube.

Mercury is abnormal in its capacity for forming multiply charged particles. A study of its remarkable parabolas<sup>3</sup> enabled Sir J. J. Thomson to show that the atom of mercury can carry no less than eight charges, that is lose eight electrons. He gives reasons for considering that it loses all eight at once and then recaptures them one at a time, so giving rise to a series of parabolas 200/1, 200/2, 200/3, etc. The brightest is the first, which is due to atoms which have recaptured all but one electron ; the others are progressively fainter.

Subjected to the greater resolving power of the mass spectrograph it was seen at once that mercury was a complex element. Its first-, second-, third-, and higher-order lines appeared as a series of characteristic groups around positions corresponding to masses 200, 100,  $66\frac{2}{3}$ , etc. Some of these will be easily distinguished on the spectra reproduced. The second-, third- and fourth-order groups are well shown in Spectrum VIII, Plate IV. Study of the group showed the presence of a strong line at 202, a weak one at 204 and an unresolved band.<sup>4</sup> It was not until the writer's second mass spectrograph was working that the main lines were properly resolved and shown to be 198, 199, 200, 201, 202, 204.<sup>5</sup> Several photographs of the second-order group of mercury are reproduced in Plate VI. Later a very rare component 196 was identified.<sup>6</sup> In 1932 still fainter effects at 197 and 203 were

<sup>1</sup> *Nature*, **136**, 476, 1935.

<sup>2</sup> *Phys. Rev.*, **53**, 64, 1938.

<sup>4</sup> Aston, *Phil. Mag.*, **39**, 623, 1920.

<sup>5</sup> Aston, *Nature*, **116**, 208, 1925.

<sup>3</sup> *V. Plate I.*

<sup>6</sup> Aston, *ibid.*, **120**, 224, 1927.

ascribed to isotopes,<sup>1</sup> but this was disproved by the work of Bainbridge and Jordan<sup>2</sup> and the absence of these, and of other probable mass numbers, proved to a very high degree by Nier.<sup>3</sup> The relative abundance of the isotopes was first determined by photometry.<sup>4</sup> It was the heaviest element yielding mass rays easily and its group formed an invaluable reference scale of abundance for elements of similar weight. The curve of the photographic efficiency of its rays, shown in Fig. 24, indicates that it was not particularly favourable to the method, and its lines were too close together for the most reliable device, that of intermittent exposures, to be employed. The mean values then obtained from a large number of spectra are given below. More recently Nier<sup>5</sup> has measured the abundances by his much more accurate electrometric method. The constitution of mercury is as follows :

Mass number .	196	198	199	200	201	202	204
Abundance (1)	0·10	9·89	16·45	23·77	13·67	29·27	6·85
(2)	0·15	10·11	17·03	23·26	13·17	29·56	6·72

(1) Aston, 1930; (2) Nier, 1937.

In the first survey of packing fractions<sup>6</sup> that of mercury was of the greatest importance. Not only were its rays exceptionally easy to produce, but its series of multiply charged groups, unique before Dempster introduced his hot spark method, were accepted gratefully as divisions, naturally inscribed on the mass scale, which connect the highest atomic masses with the lower ones without fear of accumulated error. During the work the group could be distinguished even to the sixth order. The only method of measurement then available was by comparing the CO<sub>2</sub> line with that of triply charged <sup>198</sup>Hg by means of the known ratio of the second- and third-order lines of mercury themselves. Only one good plate was obtained which indicated a value indistinguishable from that of CO<sub>2</sub>, then taken to be 0·8.

More accurate measurements have been made with the writer's third instrument by comparison of the triply charged lines with those of doubly charged xenon.<sup>7</sup> The results are given on page 105. If these are corrected for the later values of the substandards the packing fraction of mercury becomes 1·7, according well with Dempster's curve, and giving an atomic weight 200·59 in good agreement with the chemical value 200·61.

<sup>1</sup> Aston, *Nature*, **130**, 847, 1932.

<sup>2</sup> *Phys. Rev.*, **50**, 282, 1936.

<sup>3</sup> *Ibid.*, **52**, 933, 1937.

<sup>4</sup> Aston, *Proc. Roy. Soc., A*, **126**, 523, 1930.

<sup>5</sup> *Phys. Rev.*, **52**, 933, 1937.

<sup>6</sup> Aston, *Proc. Roy. Soc., A*, **115**, 508, 1927.

<sup>7</sup> Aston, *ibid.*, **163**, 391, 1937.

81. *Thallium.*

From the statistical rule concerned with the isotopic constitution of elements of odd atomic number<sup>1</sup> and its chemical atomic weight 204.39, thallium should consist of two isotopes 203 and 205. Experimental evidence supporting this conclusion was obtained by Schuler and Keyston<sup>2</sup> who from their work on hyperfine structure deduced that two isotopes were present with a ratio of abundance estimated as 2.3 to 1. Definite proof was obtained the same year by the analysis of the slightly unstable ethyl compound by the second mass spectrograph<sup>3</sup> when lines 203 and 205 were obtained, the latter being the stronger. The presence of the lines of mercury enabled the relative abundance and also the packing fraction to be estimated.<sup>4</sup> Photometry gave the ratio of abundance as 2.40. Quite recently Nier<sup>5</sup> with his mass spectrometer has obtained 2.44 in good agreement. He has also proved the absence of other mass numbers to a very high degree.

The first estimate of the packing fraction was one unit higher than that of mercury. With the latest value of the latter this is 2.7, in agreement with Dempster<sup>6</sup> who gives the difference between thallium and palladium as  $8.03 \pm 0.2$ . With Nier's ratio of abundance the percentages, adopted in the table, are 29.1 and 70.9 and the atomic weight is 204.41, in good agreement with the international chemical value 204.39.

82. *Lead.*

As has been pointed out in Chapter II, lead is unique among the elements in being formed in workable quantities on the earth as the result of radioactive disintegrations. The isotopic constitution of radiogenic lead will obviously depend upon the particular process of its evolution, and indeed the first proof of the existence of isotopes was the fact that lead originating from uranium had a smaller atomic weight than that originating from thorium. The vast bulk of terrestrial lead does not fall into the same category. Except when contaminated with radiogenic lead it appears to have a reasonably constant isotopic constitution, and to behave generally as an ordinary complex element.

*Common Lead.* Although some faint and incompletely resolved effects were obtained by the use of finely divided metallic lead in the writer's work on accelerated anode rays<sup>7</sup> the first successful analysis

<sup>1</sup> V. p. 204.

<sup>2</sup> *Zeit. Phys.*, **70**, 1, 1931.

<sup>3</sup> Aston, *Nature*, **128**, 725, 1931.

<sup>4</sup> Aston, *Proc. Roy. Soc., A*, **134**, 571, 1932.

<sup>5</sup> *Phys. Rev.*, **54**, 275, 1938.

<sup>6</sup> *Ibid.*, **53**, 64, 1938.

<sup>7</sup> Aston, *Phil. Mag.*, **49**, 1198, 1925.

was made by his second mass spectrograph<sup>1</sup> using the discharge through the volatile tetramethyl compound. Owing to the presence of hydrogen the spectra obtained were ill defined but showed the three principal isotopes 206, 207 and 208, roughly in proportions 4 : 3 : 7. Later a fourth, 204, was discovered by Schuler and Jones.<sup>2</sup> This was confirmed in mass spectra obtained by the writer<sup>3</sup> repeating the analysis of the tetramethyl with improved vacuum technique. With the more intense beams faint effects at 203, 205, 209 and 210 were observed which at the time were thought to be due to isotopes, but were later shown to be spurious<sup>4</sup> and the photometric abundances corrected to the figures shown below. These have now been superseded by the more accurate electrometric ones of Nier whose detailed investigation<sup>5</sup> with his precision mass spectrometer shows that the relative abundances vary considerably with the sources of the common lead, but that they are constant in the samples obtained from the oldest geological minerals. The following are the percentages calculated from the ratios he gives for the latter:

Mass number . . . .	204	206	207	208
Abundance (1) . . . .	1·5	28·3	20·1	50·1
(2) . . . .	1·5	23·5	22·7	52·3

(1) Aston, 1936; (2) Nier, 1938.

The first measurement of the packing fraction of the isotopes of lead showed that they were indistinguishable from those of mercury<sup>6</sup> which is now given the value 1·7. Dempster has compared the lines of lead with those of palladium and rhodium.<sup>7</sup> From his curve on p. 108 the value for lead would be about 2. Nier points out that an arbitrary value 1·55 brings the chemical and physical atomic weights into close agreement. The present chemical value is 207·21.

*Radiogenic Leads.* The problem of the isotopic constitution of the various leads found associated with radioactive minerals, which by their variation of atomic weight gave so convincing a proof of isotopy, was one of the greatest interest. As soon as a method of analysis of ordinary lead had been found efforts were made to obtain the necessary methyl compounds of these rare leads. The first successful analysis was made with a tetramethyl of a uranium lead from Norwegian

<sup>1</sup> Aston, *Nature*, **120**, 224, 1927.

<sup>2</sup> *Naturwiss.*, **20**, 171, 1932.

<sup>3</sup> Aston, *Proc. Roy. Soc., A*, **140**, 535, 1933.

<sup>4</sup> Aston, *Nature*, **137**, 613, 1936.

<sup>5</sup> *Phys. Rev.*, **53**, 680; *J. Amer. Chem. Soc.*, **60**, 1571, 1938.

<sup>6</sup> Aston, *Proc. Roy. Soc., A*, **140**, 535, 1933.

<sup>7</sup> *Phys. Rev.*, **53**, 64, 1938.

Broggerite prepared at the Geophysical Laboratory, Washington.<sup>1</sup> This was analysed by the writer with his second mass spectrograph.<sup>2</sup> The spectra were very faint and indistinct owing to the hydrogen in the camera, but lines 206, 207, 208 were visible and their intensities were estimated photometrically to be 100, 10·7, 4·5. At the time there was no reason to suppose that these could be affected by the presence of a hydride, so the percentages were worked out to be 86·8, 9·3, 8·9.

The presence and intensity of line 207 were of fundamental interest. As it was much stronger than line 208 it could not be due to the presence of ordinary lead as an impurity, for in ordinary lead 208 is more than twice as strong as 207, neither could it be the product of the disintegration of radium or thorium. There was, therefore, every reason to identify it as the end product of the only other known disintegration series, namely that of actinium. This settles the mass numbers of all the members of the series, that of protactinium being 231. Assuming the ratio of 100 : 7 for the number of atoms of uranium lead to actinium lead Lord Rutherford<sup>3</sup> was able to work out the period of actino-uranium, the parent of the actinium series, and an isotope of uranium, to be  $4\cdot2 \times 10^8$  years, and deduce other important cosmical conclusions.

Further knowledge of the isotopic constitution of radiogenic leads was highly desirable in connection with the problems of geologic time and the origin of actinium. Dr. A. v. Grosse, who was particularly interested in the latter problem, undertook the preparation of the methyls of a variety of rare radiogenic leads and these were then analysed by means of the writer's second mass spectrograph and the relative abundance of the isotopes estimated photometrically.<sup>4</sup> The problem was complicated by the presence of lines due to hydrides, the intensity of which had to be estimated and allowed for. The results, which were in good agreement with the chemical atomic weights concerned, are included in the table given below. Later analyses were made by Rose and Stranathan,<sup>5</sup> and Mattauch and Hauk,<sup>6</sup> and a very complete investigation was undertaken by Nier.<sup>7</sup> In this important publication, from which Table XII is taken, the analyses of a large number of radiogenic leads are recorded, and the connection between these and the problem of geological time fully discussed.

<sup>1</sup> Piggot, *J. Acad. Sci.*, **18**, 269, 1928.

<sup>2</sup> Aston, *Nature*, **123**, 313, 1929.

<sup>3</sup> *Nature*, **123**, 313, 1929.

<sup>4</sup> Aston, *Proc. Roy. Soc., A*, **140**, 535, 1933.

<sup>5</sup> *Phys. Rev.*, **50**, 792, 1936.

<sup>6</sup> *Naturwiss.*, **25**, 763, 1937.

<sup>7</sup> *Phys. Rev.*, **55**, 150, 1939.

TABLE XII

RELATIVE ABUNDANCE OF ISOTOPES IN RADIogenic LEADS DETERMINED BY DIFFERENT OBSERVERS

Mineral.	Observer.	Isotope Abundance.			
		204	206	207	208
{ Pitchblende Great Bear Lake	Aston . .		100	8.8	2.56
	R. and S. .		100	9.46	3.15
	Nier . .	0.062	100	9.75	2.53
{ Pitchblende Katanga, Africa	Aston . .		100	7.18	0.02
	R. and S. .		100	6.74	0.3
	M. and H.		100	5.15	
	Nier . .	0.006	100	6.08	0.077
{ Uraninite Wilberforce, Canada	Aston . .		100	9.66	6.75
	R. and S. .		100	8.32	7.17
	Nier . .	0.011	100	7.49	6.16
{ Uraninite Morogoro, Africa	Aston . .		100	7.42	0.0
	Nier . .	0.001	100	5.98	0.18
{ Thorite Brevig, Norway	Aston . .		4.88	1.38	100
	Nier . .	0.061	5.53	1.22	100

### 83. *Bismuth.*

The first result with this element was obtained with accelerated anode rays.<sup>1</sup> Metallic bismuth was ground into the anode paste, and after a long exposure, with the anode worked at a white heat, it gave a single line at the place expected from its atomic weight 209.00. This result was confirmed by Bainbridge and Jordan,<sup>2</sup> and more recently Nier<sup>3</sup> has showed that bismuth is simple to a very high degree indeed. Dempster<sup>4</sup> has measured the difference of its packing fraction from that of palladium as  $7.84 \pm 0.1$ , and estimates that of bismuth at rather greater than 2. This value will almost compensate for the change from the physical to the chemical scale, so that the chemical atomic weight 209.00 is in excellent agreement with the mass spectrum results.

<sup>1</sup> Aston, *Phil. Mag.*, **49**, 1197, 1925.

<sup>2</sup> *Phys. Rev.*, **50**, 282, 1936.

<sup>3</sup> *Ibid.*, **54**, 275, 1938.

<sup>4</sup> *Ibid.*, **53**, 72, 870, 1938.

***84. Polonium.***

No stable isotopes known. For radioactive isotopes see p. 13.

***85. (Eka-iodine).***

Not identified as occurring naturally.

***86. Radon, Actinon, Thoron.***

No non-radioactive isotope corresponding to this atomic number is known. It is clear that if such a substance is capable of existence it should be present in the atmosphere, its mass number should lie between 210 and 230 and its boiling point will be that of radon, namely  $-65^{\circ}\text{C}$ . A critical search was made for it in 1923.<sup>1</sup> Fourteen years earlier the late Sir James Dewar had collected in charcoal the least volatile fractions from 439 tons of liquid air. These residues were purified and fractionated in a long series of operations down to a volume of 0.02 c.c., which should have contained practically the whole of the unknown element if present. This was analysed in the first mass spectrograph but failed to show any indication of lines in the region expected. From this result it was inferred that if a heavier inert gas exists in the atmosphere it is certainly not present to the extent of 1 in  $10^{15}$  and probably not to the extent of 1 in  $2 \times 10^{16}$  parts by volume.

No mass spectra have yet been obtained with the known radioactive isotopes. Actinon is certainly, and thoron probably, too rare for the purpose. Radon could indeed be used to give its mass line 222 by introducing it into the discharge, but so far this has not been done, for the practical reason that the mass spectrograph would probably be ruined for further work owing to the radioactive contamination involved.

***87. (Eka-cæsium.)***

Many efforts have been made in the past to demonstrate the existence of this element. The methods of mass spectrum analysis were applied to the problem in 1929 by Bainbridge<sup>2</sup> who used a special form of Dempster magnetic spectrograph for the purpose, and critically examined the region round mass number 223. In his report, to which the reader is referred for an account of previous work on the subject, Bainbridge states : " Eka-cæsium was not existent to an extent greater than  $3.5 \times 10^{-7}$  part of the cæsium from pollucite or greater than  $7.3 \times 10^{-6}$  part of the cæsium from lepidolite."

<sup>1</sup> Aston, *Proc. Roy. Soc., A*, **103**, 462, 1923.

<sup>2</sup> Bainbridge, *Phys. Rev.*, **34**, 752, 1929.

Later Papish and Wainer<sup>1</sup> made a provisional claim to have detected element 87 in samarskite by X-ray analysis. This has been supported by the work of Barnes and Gibbs<sup>2</sup> who by means of a Dempster apparatus have detected positive ions of mass (roughly) 220 in the sulphate of element 87 provided by Papish. On the other hand, Hirsh,<sup>3</sup> on re-examination of the work of Papish, concludes that the lines originally reported are due to a crystal defect. The claims of Holubei<sup>4</sup> to have detected feeble effects of element 87 in an X-ray analysis of a heavy extract from pollucite and other minerals have not been confirmed.

### 88. Radium.

No mass spectrum work has been done on this element, nor is any really necessary. It is simple, of mass number 226. Its isotopic weight can be calculated either from its parent  $^{238}\text{U}$  or its stable product  $^{206}\text{Pb}$ . In this way Dempster<sup>5</sup> gives the packing fraction of  $^{226}\text{Ra}$  as 4.6. This corresponds to an atomic weight 226.044, in good agreement with the international chemical value 226.05.

### 89. Actinium.

No stable isotope known. For radioactive isotopes see p. 13.

### 90. Thorium.

No results were obtained with this radioactive element until 1934 when it yielded to anode ray methods employed for the heavier rare earths.<sup>6</sup> One line only was observed at the expected mass number 232. This result was confirmed by Dempster<sup>7</sup> who compared the packing fraction of thorium with that of tin, and estimated the difference to be  $10.12 \pm 0.1$ . With the latest value for tin this gives 4.6 for thorium. Dempster<sup>8</sup> gives a rather higher value, 5.12. This corresponds to an atomic weight 232.05. The chemical value is 232.12.

### 91. Protactinium.

Of the possible radioactive isotopes of atomic number 91 one only, protactinium, the parent of the actinium series, has a sufficiently long life to hold out hope of accumulation in chemical quantities.

<sup>1</sup> Papish and Wainer, *J. Amer. Chem. Soc.*, **53**, 3818, 1931.

<sup>2</sup> Barnes and Gibbs, *Phys. Rev.*, **40**, 318, 1932.

<sup>3</sup> *Ibid.*, **51**, 584, 1937.

<sup>4</sup> *Compt. Rend.*, **205**, 854, 1937; **209**, 675, 1939.

<sup>5</sup> *Phys. Rev.*, **53**, 869, 1938.

<sup>6</sup> Aston, *Nature*, **133**, 684, 1934; *Proc. Roy. Soc., A*, **149**, 396, 1935.

<sup>7</sup> *Nature*, **138**, 120, 1936.

<sup>8</sup> *Phys. Rev.*, **53**, 869, 1938.

On the view that the isotope 207 found in lead from uranium<sup>1</sup> was the final product of the actinium series, the mass number of protactinium should be 231. The determination of the chemical atomic weight by Grosse<sup>2</sup> supports this conclusion and an atomic weight 231 has been adopted.

### *92. Uranium.*

Determinations of the constitution of this, the heaviest of the ordinary elements, were of great interest in connection with its radioactivity. Its properties are not favourable to mass spectrum analysis, and it was not until 1931 that results were obtained by means of its volatile hexafluoride.<sup>3</sup> One line only, of mass number 238, could be seen, and it was concluded that it was simple to at least 97 per cent. This made it highly probable that the chemical atomic weight 238·14, then in use, was too high. The expected second constituent, actinouranium, of mass number 235, was detected by Dempster<sup>4</sup> who estimated its abundance at less than 1 per cent. A third very rare isotope 234 has been recently recorded by Nier<sup>5</sup> with his mass spectrometer, this is the body called U II and known by radioactivity theory to be a constituent of uranium. Nier gives the ratio 238 : 235 as  $139 \pm 1$  per cent., and 238 : 234 as 17,000  $\pm 10$  per cent., corresponding to percentage abundance :

Mass number	234	235	238
Abundance	0·006	0·71	99·28

Quite recently the isotopes 235 and 238 have actually been isolated in detectable quantities, by analysis in a mass spectrometer of the ionized vapour of  $\text{UBr}_4$ . This remarkable technical success was achieved by Nier, Booth, Dunning and Grosse,<sup>6</sup> who were thus able to show that isotope 235 was the one responsible for the fission brought about by neutrons.

Dempster has compared the doubly charged uranium lines with those of tin and finds a difference of packing fraction of 10·5, giving for  $^{238}\text{U}$  a value 5·56 and  $^{235}\text{U}$  a value 5·3.<sup>7</sup> These combined with Nier's abundances give an atomic weight 238·04. The international chemical value is 238·07.

<sup>1</sup> Aston, *Nature*, **123**, 313, 1929.

<sup>2</sup> *J. Amer. Chem. Soc.*, **56**, 2501, 1934; *Proc. Roy. Soc., A*, **150**, 363, 1935.

<sup>3</sup> Aston, *Nature*, **128**, 725, 1931.

<sup>4</sup> *Ibid.*, **136**, 180, 1935.

<sup>5</sup> *Phys. Rev.*, **55**, 150, 1939.

<sup>6</sup> *Ibid.*, **57**, 546, 1940.

<sup>7</sup> *Ibid.*, **53**, 64, 869, 1938.

PART IV  
THEORETICAL AND GENERAL  
CHAPTER XII  
THE ELECTRICAL THEORY OF MATTER

**103. The whole number rule.**—The first and by far the most important generalization which could be made from the results obtained with the first mass spectrograph was that the weights of all atoms could be expressed as whole numbers to a high degree of accuracy. This approximation which is called the “whole number rule” enabled the most sweeping simplifications to be made in the ideas of mass and removed the only serious objection to the unitary theory of matter.

**104. The unitary theory of the constitution of matter.**—From the very earliest times it has been a favourite hypothesis that all matter is really composed of one primordial substance—Air, Fire, Earth and Water have all been suggested in the past.

The first definite theory of the constitution of the atoms of the elements out of atoms of a primordial element (Protyle, Urstoff, etc.) was made by Prout in 1815. *Prout's Hypothesis* was that the atoms of the elements were different aggregations of atoms of *hydrogen*. On this view it is obvious that the atomic weights should all be expressed by whole numbers when the atomic weight of hydrogen itself is taken as unity. Owing to the roughness of the methods available and the considerable inaccuracies of the atomic weight determinations made at that time there was little to disprove the hypothesis, and its marked simplicity gained it many adherents. But as time went on chemical methods grew more precise and it became more and more impossible to reconcile experimental results with integral combining weights until the evidence against it was strong enough to cause J. S. Stas (1860–1865) to state : “I have arrived at the absolute conviction, the complete certainty, so far as it is possible for a human being to attain to certainty in such matters, that the law of Prout is nothing but an illusion, a mere speculation definitely contradicted by experience.”

Nevertheless, though abandoned temporarily by the chemist as impracticable, the idea of primordial atoms appealed strongly to the

mind of the philosopher and the physicist. Herbert Spencer, in his hypothesis of the constitution of matter, says: "All material substances are divisible into so-called elementary substances composed of molecular particles of the same nature as themselves; but these molecular particles are complicated structures consisting of congregations of truly elementary atoms, identical in nature and differing only in position, arrangement, motion, etc., and the molecules or chemical atoms are produced from the true or physical atoms by processes of evolution under conditions which chemistry has not been able to reproduce."

The discovery of the electron, the proof that it was the same whatever the atom from which it was detached and, most important of all, the demonstration by Sir J. J. Thomson and others that electrical charges always possess the property of mass, gave us the key to the riddle of what these primordial atoms really are. The only serious obstacle, the fractional atomic weights, was removed by the whole number rule, and the simplest possible theory was adopted, namely that the atoms of the elements are themselves built of the atoms of positive and negative electricity, protons and electrons.

**105. The electron.**—This fundamental unit of negative electricity makes its appearance in physical phenomena in many guises, such as the cathode ray of electrical discharge, the beta ray of radioactive change, the thermion of the wireless valve. It is not proposed to describe its history and properties at any length here. It will be sufficient to note a few of its more important constants.

Its charge  $e$  is  $4.802 \times 10^{-10}$  E.S.U. The most reliable measurements for  $e/m$  for the electron, at low velocity, give the value  $5.273 \times 10^{17}$  E.S.U. Its mass is  $9.106 \times 10^{-28}$  grs., 1837 times less than the proton, or 0.0005486 on the physical scale of isotopic weight.

**106. The proton.**—Until quite recently the only unit of positive electricity recognized was the hydrogen positive ray of mass 1, that is to say the positively charged part remaining when an electron is detached from a neutral protium atom. The name "proton"<sup>1</sup> was suggested for it by Sir Ernest Rutherford at the Cardiff meeting of the British Association in 1920. Its charge is, of course, equal and of opposite sign to that on the electron. Its mass in the free state, from mass spectrum measurements already described, is 1.007581 on the physical scale, or  $1.6725 \times 10^{-24}$  grs.

**107. The nucleus atom.**—Certain experimental results, notably the scattering of alpha rays, led Sir Ernest Rutherford in 1911<sup>2</sup> to formulate an atom model which has resulted in remarkable advances

<sup>1</sup> From Greek *πρῶτον* first—the primary substance.

<sup>2</sup> Rutherford, *Phil. Mag.*, 21, 669, 1911.

in both physics and chemistry, and is now almost universally accepted as correct in fundamental principle. This is that an atom of matter consists of a central massive nucleus carrying a positive charge which is surrounded, at distances relatively great compared with its diameter, by "planetary" electrons. The central nucleus contains all the positive electricity in the atom, and therefore practically all its mass. The weight of the atom and its radioactive properties are associated with the nucleus; its chemical properties and spectra, on the other hand, are properties of its planetary electrons. It is clear that in a neutral atom the positive charge on the nucleus must be equal to the sum of the negative charges on the planetary electrons. There is ample literature available on the exterior structure of the atom, that is to say, that part of it consisting of planetary electrons. Modern wave mechanics has been applied to these with striking success so that it is possible, with the aid of the "exclusion principle," to explain how the periodic table is built up. These developments are, however, not necessary to explain the main attributes of isotopes for which the simplest type of Rutherford-Bohr model is adequate.

**108. The neutron.**—For many years after the discovery of the whole number rule it was supposed that the nucleus actually consisted of protons and electrons, but the theoretical difficulties of dealing with electrons as nuclear building stones became insurmountable, and the position was much clarified by the discovery, by Chadwick in 1932, of the theoretically predicted neutral particle the "neutron." This has zero electric charge and its mass has been recently estimated at  $1.00895 \pm 0.00003$ <sup>1</sup> on the physical scale. This is slightly greater than the isotopic weight of the neutral atom of protium, and in all probability the neutron has not the same quality of stability as have the proton and electron. It cannot exist indefinitely in a free state, but will spontaneously disintegrate into these particles with the liberation of energy. Whether we look upon a neutron as being composed of a proton and an electron, or not, is, according to modern nuclear theory, quite immaterial, but there seems no doubt that in the nucleus of the atom it behaves, and must be treated, as a single entity. All normal nuclei of atoms are now regarded as being built of protons and neutrons only, and the difficulty of beta ray production is got over by supposing that the electron is only born in the radiating nucleus at the moment of its expulsion.

The simplest composite nucleus is that of deuterium which will consist of one proton plus one neutron. This is called a deuteron and is of enormous importance as a projectile in artificial atomic transmutations.

<sup>1</sup> Mattauch, *Zeit. tech. Phys.*, **12**, 582, 1938.

Other particles recently discovered, such as the "positron" or positive electron, the "meson" intermediate in mass between the proton and the electron, and such hypothetical entities as "neutrinos," are not essential in the explanation of the general properties of isotopes, the atoms of which can be simply illustrated as being built of three constituents, electrons, protons and neutrons.

**109. Diagrammatical representation of atoms of isotopes and isobars.**—The accompanying diagrams (Fig. 37) are intended

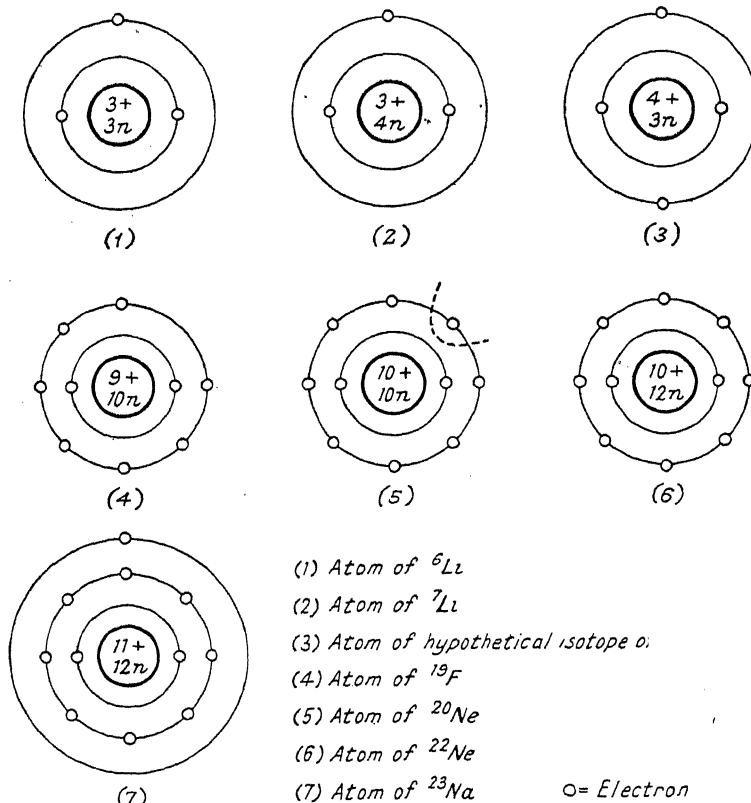


FIG. 37.—Diagrammatic Representation of Nucleus Atoms. The planetary electrons are shown as lying on plane circles, the first containing 2, the second 8 and so on. (1) and (2) are Isotopes. (2) and (3) are Isobars and (5) and (6) are Isotopes.

to indicate the sort of arrangement which may take place in atoms. The small dark circle is the nucleus, the number of protons (+) and neutrons (*n*) comprising it being indicated by the numerals. The electrons outside the nucleus are indicated by small light circles.

(1) is an atom of atomic weight 6. Its nucleus contains 3 protons

and 3 neutrons, hence its atomic number is 3. It is in fact the atom of the lighter isotope of lithium of atomic weight 6,  $^6\text{Li}$ . To be electrically neutral it must have 3 electrons outside the nucleus. The first two of these electrons will form an innermost ring or shell of two. This shell being now complete, any more electrons will go outside and start the next shell of eight, so we indicate this by putting the third electron in a circle of greater diameter.

Now suppose we add one electron and one proton to this atom. If both as a neutron enter the nucleus we shall get the configuration represented by (2). The nuclear charge is unaltered, so that the arrangement of the exterior electrons will be precisely the same. It follows that all properties depending on these electrons such as atomic volume, spectrum, chemical properties, etc., will be quite unaltered. But the weight of this atom is now 7, so it is an isotope of lithium; it is actually the atom of the heavier constituent  $^7\text{Li}$ .

(1) AND (2) ARE ISOTOPES.

But now suppose we add a proton and an electron to (1) so that the proton only enters the nucleus and the electron remains outside as shown at (3). We shall now have a charge 4 on the nucleus and two electrons in the outer ring. The chemical properties of such an atom, if it could exist, would be completely different from those of lithium, but would be identical with those of beryllium, of which it would be an isotope. But its mass is clearly identically the same as that of (2) so that (2) AND (3) ARE ISOBARS.

In the same way (4) will be recognized as the atom of fluorine, (5) and (6) as the atoms of the two isotopes of neon and (7) as the atom of sodium.

**110. The relation between isotopes and elements in the same group.**—As far as can be seen the chemical properties by which the elements are divided into groups depend practically entirely on the outermost shell of electrons, which are therefore called valency electrons. Now consider all that part called the core of the atom lying within the shell of these valency electrons. The movements of the outermost electrons will depend in the first degree on the charge on the core, which may be looked upon as a virtual nucleus. The cores of atoms (1) and (7) both have the same net charge 1, so that the elements they represent should have many chemical similarities. These they certainly have as both are alkali metals. In general, the atoms of elements belonging to the same group chemically have the same number of electrons in the outer shell, and the same net charge on the core. Chemical similarity is carried a stage further in the triad groups of the transition elements such as iron, cobalt and nickel. In these not only is the charge on the core the same,

but also the construction of the outer shell of the core is closely similar for all these elements. In the group of trivalent rare earths the similarity extends even deeper and the construction of two shells of the core hardly varies within the group so that chemical differentiation is now so feeble that the elements can only be separated from each other with the greatest difficulty. The final stage of similarity is reached in isotopes where the nuclear charge being the same chemical differences vanish for all practical purposes.

**111. Abnormal compounds formed by charged atoms.**—The tendency of elements to form compounds with each other, that is the property with which the idea of valency is associated, is ascribed to the tendency of the atom to complete its outer shell. This it can do either by parting with the electrons in this shell and so promoting the next inner completed shell to the outer position, or by sharing the electrons in the atom of another element so that they fill the gaps in its own outer shell. This idea of electron sharing has been of great value in explaining valency and the properties of chemical compounds. For the present argument it will be enough if it is understood that lithium and sodium (1) (2) (7) will very readily part with their solitary valency electron and become positively charged, i.e. will be strongly electropositive elements with valency + 1; whereas a fluorine (4) will have an equally powerful tendency to take up an electron and become negatively charged and so will be a strongly electronegative element with valency - 1. Both of these tendencies will be satisfied if (4) and (7) combine forming the compound molecule NaF, for the outer electron of (7) will enter the outer shell of (4) thus forming two complete shells of eight. We trace the tendency of the atom of fluorine, or any other halogen, to form compounds with the atom of an electropositive element, or with the atom of hydrogen, to the fact that it has one electron too few in its outer shell.

Now the only way we can give a positive charge to an atom of neon (5) or (6) is by knocking one or more electrons out of its outer shell. Suppose we remove one from (5) as indicated by the dotted line. (5) now will have a similar outer shell to (4) and a valency - 1, so we may expect that atoms of the inert gases carrying a single positive charge will behave chemically in a similar manner to neutral halogen atoms and will therefore be capable *so long as they are charged* of forming hydrides. This important idea was first suggested by Sir J. J. Thomson in connection with the charged atoms of chlorine<sup>1</sup> and certainly supplies a very satisfactory explanation of the abnormal hydrides of inert gases and compounds such as OH<sub>3</sub> discovered in

<sup>1</sup> J. J. Thomson, *Proc. Roy. Soc., A*, **99**, 90, 1921.

positive rays. The line at 41 (Spectrum VI, Plate III) is probably to be put down to a charged hydride of argon of this type. In the case of atoms carrying more than one charge it can be generally stated that each positive charge given to an atom will increase its negative valency by one. This behaviour in positive rays should not be entirely unexpected by the chemist, for it is clearly similar to the formation of positively charged ions such as  $\text{NH}_4^+$  which are well known in the chemistry of solutions.

**112. Failure of the additive law with regard to mass.**—For velocities small compared with that of light the masses of the constituent particles may be regarded as universal constants, and if the additive law of mass held as accurately when an atom is built up of them as when, for instance, a molecule is built of atoms the divergences from the whole-number rule would be too small to be significant, and the masses of all atoms would be whole numbers on the scale  $H = 1$ . The measurements made with the first mass spectrograph were sufficiently accurate to show that this was not true. The theoretical reason adduced for this failure of the additive law is that, inside the nucleus, the protons and neutrons are packed so closely together that their electromagnetic fields interfere and a certain fraction of the combined mass is destroyed, whereas outside the nucleus the distances between the charges are too great for this to happen. The mass destroyed corresponds to energy released, analogous to the heat of formation of a chemical compound, the greater this is the more tightly are the component charges bound together and the more stable is the nucleus formed. It is for this reason that measurements of this loss of mass are of such fundamental importance, for by them we may learn something of the actual structure of the nucleus. On the view that the nucleus consists entirely of protons and neutrons it is obvious that the atomic number of the atom is equal to the number of protons, whereas the mass number is the sum of the numbers of protons and neutrons. The difference between the total mass of the constituent particles, when added up, and the actual mass is called the "binding energy" of the nucleus, and is a direct measure of its stability.<sup>1</sup>

**113. Standard of mass.**—As soon as it was found possible to measure the masses of atoms to a high degree of accuracy it became necessary to decide upon a suitable unit of mass. At the time the first high-precision measurements were made oxygen was regarded as a simple element and its line 16 was very naturally adopted as a

<sup>1</sup> For further information on current views of the structure of atomic nuclei the reader is referred to : Feather, *An Introduction to Nuclear Physics*, Cambridge, 1936.

standard of reference and the mass corresponding to one-sixteenth of the neutral atom  $^{16}\text{O}$  was taken as unity.

When the complexity of oxygen was discovered and it became clear that this unit differed from the classical chemical one—one-sixteenth of the mean oxygen atom—the matter had to be reconsidered. At a discussion on the subject at the meeting of the British Association in 1931 it was urged<sup>1</sup> that the chemical standard should remain as before. It gives a scale upon which many of the most frequently occurring elements are sufficiently close to whole numbers for all ordinary calculations of analysis. From the purely chemical view the discovery of the complexity of oxygen is clearly of little importance. The actual sub-standards of atomic weight determination, chlorine, bromine and silver have long been known to be complex to a much more serious degree. As, in all probability, most chemists will be dealing for an indefinite time to come with the present mixed but constant quality of complex elements it seems needless to alter a standard which has figured in chemical literature for so long a time.

For physical purposes it is essential that the unit should be founded on some definite species of atom which can be recorded on a mass spectrum. Logically the hydrogen atom of mass number 1 would at first sight appear the natural unit, but although this would make all the packing effects of the same sign it is practically inadmissible since it throws the masses of the heavy atoms right off their proper mass numbers. The scale  $^4\text{He} = 4$  avoids this defect and was suggested as the only possible identical physical and chemical one.<sup>2</sup> It is now certain that helium is simple to quite a high enough degree,<sup>3</sup> but it cannot be used as a practical chemical standard for obvious reasons. Its density is not easy to fix and for the purposes of the mass spectrograph it is too near the low end of the scale. It is questionable if the possible advantages of its adoption would offset the wholesale alteration of all accepted atomic weights, though this was actually carried out by Gamow. For comparison of atomic masses by the physical methods of band spectra, mass spectra and artificial transmutation the neutral atom of oxygen of mass number 16 is now generally accepted as the fundamental standard. It may be regarded as consisting of a nucleus built of 8 protons and 8 neutrons surrounded by 8 planetary electrons. Incidentally it is by far the most abundant species of atom in that part of the universe now accessible to the chemist. On this "physical scale" the unit is almost exactly  $1.66 \times 10^{-24}$  grs., and the mass of any neutral atom expressed on it

<sup>1</sup> Aston, *Brit. Assoc. Report*, 333, 1930.

<sup>2</sup> Grosse, *Zeit. Phys. Chem.*, 10, 395, 1930.

<sup>3</sup> V. p. 122.

is called its "isotopic weight." As already noted (p. 80) the percentage divergence of this from a whole number, expressed in parts per 10,000 is called the "packing fraction," and represents the mean gain or loss per nuclear particle when the nuclear packing is changed from that of  $^{16}\text{O}$  to that of the atom in question. For the measurements of mass by the doublet method the molecules of hydrocarbons are particularly valuable, and for this reason the atoms of  $^1\text{H}$ ,  $^2\text{D}$  and  $^{12}\text{C}$  are adopted as sub-standards.

**114. Transmutation and sub-atomic energy.**—Two results which were first demonstrated by the mass spectrograph, firstly the whole-number rule, which showed the high probability of all atoms being composed of the same ultimate units, and secondly the fact that one helium atom does actually weigh less than four hydrogen atoms have profound and far-reaching theoretical implications.

On Einstein's Theory of Relativity mass and energy are interchangeable and in C.G.S. units a mass  $m$  at rest may be expressed as a quantity of energy  $mc^2$ , where  $c$  is the velocity of light. This proposition has now received experimental proof by the comparison of the energy of the alpha particles released, with the mass lost in the nuclear reaction when an atom of  $^7\text{Li}$  is disintegrated by proton bombardment.<sup>1</sup> Owing to the high value of  $c$ , even in the case of the smallest mass this energy is enormous. The loss of mass when a single helium atom is formed from four hydrogen atoms amounts in energy to that acquired by a charge  $e$  falling through a potential of nearly thirty million volts. If instead of considering single atoms, we deal with quantities of matter in ordinary experience, the figures for the energy become prodigious.

Take the case of one gramme atom of hydrogen, that is to say the quantity of hydrogen in 9 c.c. of water. If this is entirely transmuted into helium the energy liberated will amount to about  $6.5 \times 10^{18}$  ergs or 200,000 kilowatt hours. This transformation of mass into radiation by the partial or complete annihilation of matter is the so-called "sub-atomic energy" and was long ago evoked as the probable source of the heat of the stars, and a possible boundless store of energy for human consumption, when it could be released and controlled.

In astrophysics the source of energy most favoured by theory was the degradation of hydrogen to helium, and the baffling question of the mechanism by which this might be brought about has recently been most elegantly solved by Bethe<sup>2</sup> who, after considering a great number of chain reactions, shows that at temperatures such as are

<sup>1</sup> V. p. 85.

<sup>2</sup> *Phys. Rev.*, 55, 434, 1939.

supposed to occur at the centre of the sun, the following series of six may be expected to take place :



Here the  ${}^{12}\text{C}$  atom is seen to act as a catalyst for the transformation of hydrogen into helium, and during the complete cycle two positrons and energy amounting to about thirty million electron volts are released.

The energy release per atom is even greater in the case of the recently discovered fission of uranium by neutrons, and, owing to the large difference between the packing fractions of uranium and those of the lighter atoms produced, may amount to about 200 million electron volts. The possibilities of artificial chain reactions of this kind have been eagerly explored in the hope of discovering a super-explosive. Fortunately there are some indications that the quantities of uranium needed would be impracticable.<sup>1</sup> The rapid advance in our powers of producing, by cyclotrons and other physical means, rays of disintegrating potentiality gives good grounds for the hope that the production and control of sub-atomic energy may be expected in the not too distant future.

<sup>1</sup> Perrin, *Compt. Rend.*, **208**, 1394, 1939.

## CHAPTER XIII

### ISOTOPE STATISTICS

**115. The relation between chemical atomic weight and atomic number.**—The importance of the chemical atomic weight has been greatly reduced by the discovery of isotopes as it is now

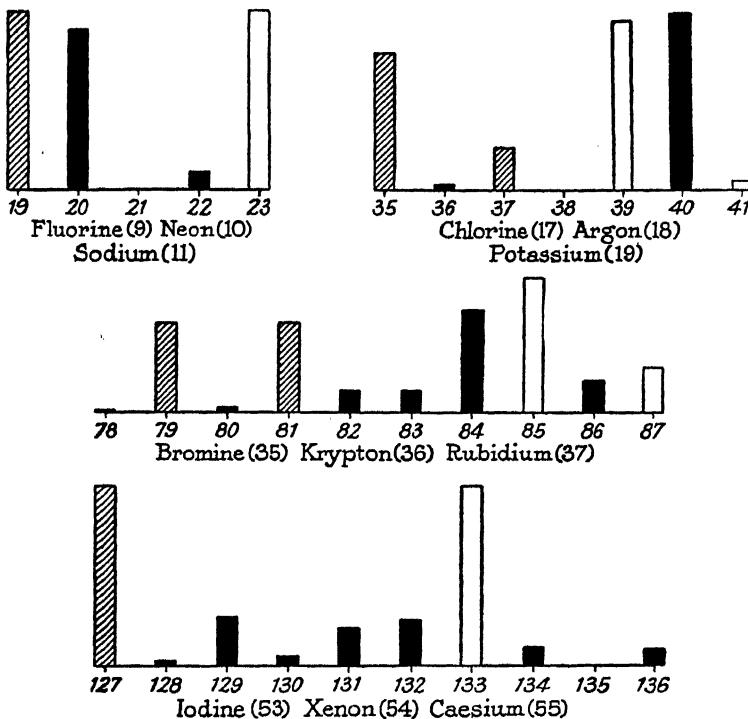


FIG. 38.—Isotopes of the Halogens, the Inert Gases and the Alkali Metals.

recognized to be in general merely a statistical mean value. Its position as the natural numerical constant associated with an element has been taken by the atomic number, though from the point of view of chemical analysis the chemical atomic weight is just as important as ever.

The possibility of anomalies in the order of the elements in the periodic table, when their chemical atomic weights are considered, is now obvious enough. The true weights of the atoms as directly determined, are so intermingled in the order of the natural numbers and the proportions present in complex elements so varied that such anomalies are bound to occur, indeed it is rather surprising there are not more.

The table (Fig. 38) shows the masses of the isotopes of three groups of elements now completely investigated. The approximate proportions present are indicated by the heights of the columns; plain for the alkali metals, black for the inert gases, and hatched for the halogens. The anomalous order of argon and potassium is at once seen to be due to the fact that whereas the heavier constituent of argon is present in much the greater proportion, in potassium the reverse is the case. Had the proportions of heavier and lighter isotopes been similar in each case the atomic weight of potassium would have been greater instead of less than that of argon.

**116. Statistical relations exhibited by elements and their isotopes.**—As the analysis of the elements proceeded interesting relations of various kinds were noted among the many species of atom disclosed. So far as stable naturally occurring elements are concerned this work is now complete. The isotopes identified by mass spectrum analysis and included in the international table are shown in the diagram Fig. 39. Subject to certain conventional restrictions with regard to stability,<sup>1</sup> 83 elements are concerned, of which 22 appear to be simple. In all 284 isotopes are tabulated and it is an astonishing fact that for practically every natural number up to 209 a stable elementary atom is known. Some of the more important relations may be stated in the form of rules as follows:

*In the nucleus of an atom there is never less than one neutron to each proton.*—Protium, the nucleus of which is not composite, is the only exception to this rule, which is the expression of the fact that if an element has an atomic number  $Z$  the mass number of its lightest isotope cannot be less than  $2Z$ . Mass numbers corresponding to  $2Z$  are known in the majority of the lighter elements up to  $^{40}\text{Ca}$ . Among the heavier elements the difference between the weight of the lightest isotope and the value  $2Z$  tends to increase with atomic weight. The corresponding divergence of chemical atomic weight from the value  $2Z$  has, of course, been noted from the beginning of the idea of atomic number.

*The number of isotopes of an element, and their range of mass number appear to have definite limits.*—Since the atomic number only depends

<sup>1</sup> V. p. 117.

H	D	He	He	Li	Li	Be	B	B	C	C	N	N	O	O	O	F	Ne	Ne	Ne		
1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22

									S							Ca					
Na	Mg	Mg	Mg	Al	Si	Si	Si	P	S	S	S	Cl	A	Cl	A	K	A	K	Ca	Ca	Ca
23	24	25	26	27	28	29	30	31	32	33	34	35	36	37	38	39	40	41	42	43	44

Ti	Ti	Cr		Fe	Co	Ni		Zn													
Sc	Ca	Ti	Ca	Ti	Ti	V	Cr	Cr	Mn	Fe	Fe	Fe	Co	Ni	Ni	Ni	Cu	Ni	Cu	Zn	
45	46	47	48	49	50	51	52	53	54	55	56	57	58	59	60	61	62	63	64	65	66

Ge		Se	Se	Kr	Kr	Kr	Sr	Sr													
Zn	Zn	Ga	Zn	Ga	Ge	Ge	As	Ge	Se	Se	Br	Se	Br	Se	Kr	Kr	Rb	Kr	Rb	Sr	
67	68	69	70	71	72	73	74	75	76	77	78	79	80	81	82	83	84	85	86	87	88

			Ru																		
Mo	Mo	Mo	Mo	Ru	Ru	Rh	Pd	Pd	Cd												
Y	Zr	Zr	Zr	Nb	Zr	Mo	Zr	Mo	Mo	Ru	Mo	Ru	Ru	Rh	Ru	Pd	Pd	Ag	Pd	Ag	Pd

					Te											Ba						
Sn	In	Sn	Sn	Sn	Te	Te	Te	Xe														
Cd	Cd	Cd	Cd	In	Cd	Sn	Sn	Sn	Sn	Sn	Sb	Sn	Sb	Sn	Te	Te	I	Te	Xe	Te	Xe	Xe

		Ce																			
Ba	Ba	Ce																			
Cs	Xe	Ba	Xe	Ba	Ba	La	Ce	Pr	Ce	Nd	Nd	Nd	Nd	Sm	Nd	Sm	Nd	Eu	Sm	Eu	Sm

																	Hf			
Dy	Dy	Er	Er															Lu		
Gd	Gd	Gd	Tb	Gd	Dy	Dy	Dy	Ho	Er	Er	Er	Er	Tm	Er	Yb	Yb	Yb	Lu	Yb	

W		Os	Os	Os										Pt		Hg	Hg			
Hf	Hf	Hf	Hf	Ta	W	W	W	Re	W	Re	Os	Os	Os	Ir	Os	Ir	Pt	Pt	Au	Pt

Pb																			
Hg	Hg	Hg	Hg	Tl	Hg	Tl	Pb	Pb	Pb	Pb	Bi								

Th														U	U	U					
221	222	223	224	225	226	227	228	229	230	231	232	233	234	235	236	237	238	239	240	241	242

Fig. 39.—The first 242 Natural Numbers showing those occupied by Mass Numbers of Known Elements.

on the net charge on the nucleus, and this will not be altered by the addition of an indefinite number of neutrons, there is no arithmetical reason why an element should not have any number of possible isotopes. The largest number known with certainty is ten in the case of tin. This is followed by xenon with nine, cadmium and tellurium with eight, and a large number of elements with seven each. The maximum difference between the lightest and the heaviest mass number is twelve units in the case of tin and xenon. If this is expressed as a proportional difference there is an exceedingly curious tendency for the spread of the isotopic groups to approximate to a limit of ten per cent., as with boron, neon, argon, krypton and tin. Hydrogen, lithium, sulphur and calcium are the exceptions which exceed this.

*Elements of odd atomic number never have more than two stable isotopes.*—This rule was noted by the writer early in the work.<sup>1</sup> It is perhaps the most remarkable of all and has no exception. Beyond atomic number 9, and with the solitary exception of lutecium, the mass numbers of the isotopes are all odd and differ by two units. In the great majority of cases the lighter is the more abundant.

*The number of neutrons in the nucleus tends to be even.*—This rule expresses the fact that in the great majority of cases even atomic number is associated with even mass number, and odd with odd. This is clearly indicated in Table XIII :

TABLE XIII

	Number of Elements.	Odd Mass Number.	Even Mass Number.	Total Isotopes.	Average Number of Isotopes.
Odd At. No. .	40	55	6	61	1·5
Even At. No. .	43	56	167	223	5·0
	83	111	173	284	3·4

The distribution of odd mass numbers is fairly even throughout the elements, but that of even mass numbers shows an extreme disparity. The mass numbers not obeying this rule are all those of weak isotopic components with the exception of  $^9\text{Be}$ ,  $^{14}\text{N}$  and  $^{129}\text{Xe}$ . Beryllium and nitrogen are the only elements consisting almost entirely of atoms whose nuclei contain an odd number of neutrons. Odd mass numbers are much scarcer than even ones both in numbers and abundance. Only one element, tin, with 115, 117 and 119 all well established, has more than two odd-numbered isotopes.

<sup>1</sup> Aston, *Phil. Mag.*, 45, 400, 1923.

*Isobaric pairs and triplets.*—Isobars, that is to say atoms having the same mass numbers but different atomic numbers, are now known in large numbers as can be seen in the diagram. In the early work many were overlooked, for in general one at least is a rare type. It will be noticed that in the majority of cases the atomic numbers of the elements forming the pairs are even and differ in each case by two units, and that the common mass number is also even. The most remarkable and important pair is argon calcium, which was the first to be discovered. This is unique in that it consists of the two preponderant isotopes of its constituent elements. These, so far from being particularly rare in Nature, are actually the most abundant inert gas and alkaline earth respectively. The third isobar  $^{40}\text{K}$  was only discovered recently and is in fact radioactive.

The extreme rarity of isobars of odd mass number was pointed out by the writer in 1933.<sup>1</sup> Taken with the previously formulated rule about elements of odd atomic number stated above, this automatically implies a corresponding rarity of isobars differing by one unit of atomic number. This has since been restated, on theoretical grounds, by Mattauch,<sup>2</sup> who went further to suggest that stable isobars of adjacent elements were incapable of existence. The stability of  $^{113}\text{Cd}^{113}\text{In}$ ,  $^{115}\text{In}^{115}\text{Sn}$  and  $^{123}\text{Sb}^{123}\text{Te}$  seems to have been established beyond doubt,<sup>3</sup> but the general argument has recently been advanced to throw doubt on the existence of the rare isotopes  $^{57}\text{Co}$  and  $^{101}\text{Rh}$ .

Isobaric triplets are, as is to be expected, of rare occurrence, the first discovered was that at mass number 96, of which all three members are now known to be stable. The others shown are also well authenticated.

*Isotopic number.*—The difference between the mass number of an atom and twice its atomic number has been called by Harkins the “isotopic number” of the atom; it is 0 for many of the light atoms and rises to a maximum 54 which is the value he allots to uranium. He has discussed the relation between natural abundance and isotopic number<sup>4</sup> and shows that atoms of isotopic number 0, such as  $^{12}\text{C}$ ,  $^{16}\text{O}$ ,  $^{24}\text{Mg}$ , etc., predominate in a marked degree. Abundance is much less for isotopic number 1 such as  $^{19}\text{F}$ ,  $^{23}\text{Na}$ ,  $^{27}\text{Al}$ , decreases again for 2:— $^{14}\text{N}$ ,  $^{22}\text{Ne}$ , and becomes practically zero for 3:— $^{37}\text{Cl}$ . Later<sup>5</sup> he gave a valuable table of known and hypothetical isotopes.

<sup>1</sup> Aston, *Mass Spectra and Isotopes*, p. 175.

<sup>2</sup> *Zeit. Phys.*, **91**, 361, 1934. <sup>3</sup> V. p. 111.

<sup>4</sup> Harkins, *Nature*, **107**, 202, 1921.

<sup>5</sup> Harkins, *J. Franklin Inst.*, **194**, 645, 1922; *J. Amer. Chem. Soc.*, **45**, 1426, 1923.

This is in the form of a diagram in which the isotopic numbers of all atomic species known and probable against their atomic numbers are plotted. They lie on a band of roughly parabolic curvature which widens as it gets further from the origin.

**117. Periodic systems of nuclei.**—The extra-nuclear properties of atoms, that is to say their chemical and spectroscopic ones, have enabled them to be classified in the well-known Periodic Table of the elements the numerical relations of which are now well understood and explained. No such table can yet be formulated to express the purely nuclear properties of atoms.

The study of stable isotopes has revealed only one definite periodicity, the apparent limit of the number of isotopes of odd elements. Examination of the mass numbers tabulated on page 203 shows an extraordinarily large number of cases in which a difference of mass number 44 is connected with a difference of atomic number 18 to give atoms having similar chemical properties such as  $^{35}\text{Cl}$   $^{79}\text{Br}$ . In the same way in the longer period 88 is connected with 32 as with  $^{93}\text{Nb}$ ,  $^{181}\text{Ta}$ .

A great many types of tabulation of mass numbers have been suggested by different investigators as a means of exploration and to suggest possible new isotopes. The work of Harkins has already been mentioned. Russell<sup>1</sup> endeavoured to associate, in occurrence and abundance, all known types of atoms with those formed in known and hypothetical radioactive disintegration series. Later a scheme devised by Urey<sup>2</sup> led him to search for isotopes of hydrogen and Johnston<sup>3</sup> by a tabulation dividing mass numbers into groups  $4n$ ,  $4n + 1$ ,  $4n + 2$ ,  $4n + 3$ , predicted many new species. A few of these have since been discovered, but in connection with selenium he was quite definitely wrong, as was Russell in predicting that molybdenum would be simple.

The success of more modern predictions has already been noted in Part III,<sup>4</sup> but these and other modern advances have taken place in connection with transmutation and the production of unstable artificial isotopes with which this book is not primarily concerned.

**118. The relative abundance of elements.**—The great disparity in the abundance of different elements in terrestrial and other cosmic matter has long been a problem of the greatest interest and is one of the few possible sources of information for formulating theories of the evolution of the elements themselves. An enormous number of chemical analyses of igneous rocks and other geological material

<sup>1</sup> Russell, *Phil. Mag.*, **47**, 1121; **48**, 365, 1924.

<sup>2</sup> Urey, *J. Amer. Chem. Soc.*, **53**, 2872, 1931.

<sup>3</sup> Johnston, *ibid.*, 2866, 1931; **54**, 824, 1932.

<sup>4</sup> V. p. 173.

have been accumulated in the past and the results tabulated. During recent years, however, the much more powerful and convenient method of X-ray analysis has been applied by Hevesy, Noddack and others to the problem with noteworthy success. It is now found that the estimates of the rarer and less-known elements are in most cases much too low, no doubt owing to the extreme difficulty of separating and estimating them by purely chemical methods. For a complete account of the latest conclusions on the abundance of elements in terrestrial and stellar matter the reader is referred to the recent work of Hevesy.<sup>1</sup>

The most obvious points to be noticed in tables of abundance are that the heavier elements are much more rare than the lighter ones and, as was first pointed out by Harkins,<sup>2</sup> that elements of even atomic number predominate to a very marked extent not only in the earth's crust, but also in such extra-terrestrial matter as meteorites. Harkins' rule is beautifully illustrated by the relative abundance of the rare earth elements as determined by X-ray analyses.

One point of obvious interest brought out is the extraordinary scarcity of the inert gases. As compared with other elements their abundance on the earth appears to be nearly a million times too small. It is difficult to resist the conclusion<sup>3</sup> that this abnormality must in some way be connected with the absence of any properties enabling them to be fixed in chemical combination.

Clearly the greatest difficulty in obtaining numerical values of relative abundance which may be used for theoretical purposes is that of defining a fair sample. The Earth taken as a whole may possibly be such, but since the vast mass of its interior is inaccessible, and processes of physical and chemical segregation of the elements have been going on presumably ever since it separated from the Sun, it cannot be regarded as a satisfactory one.

**119. The relative abundance of isotopes.**—In contradistinction to the chemical problem the determination of the ratios of abundance of constituents of the same element by mass spectrum analysis is virtually free from the uncertainty of sampling. At the time that measurements of abundance by photometry were started it was known that the relative abundance of the isotopes of a complex element showed little variation in nature. Since the discovery of isotopes among the stable elements hundreds of analyses had been made to test the unvarying nature of the atomic weights of naturally occurring

<sup>1</sup> Hevesy, *Chemical Analysis by X-rays and its Applications*, McGraw-Hill, New York, 1932.

<sup>2</sup> Harkins, *J. Amer. Chem. Soc.*, **39**, 856, 1917.

<sup>3</sup> Aston, *Nature*, **114**, 786, 1924.

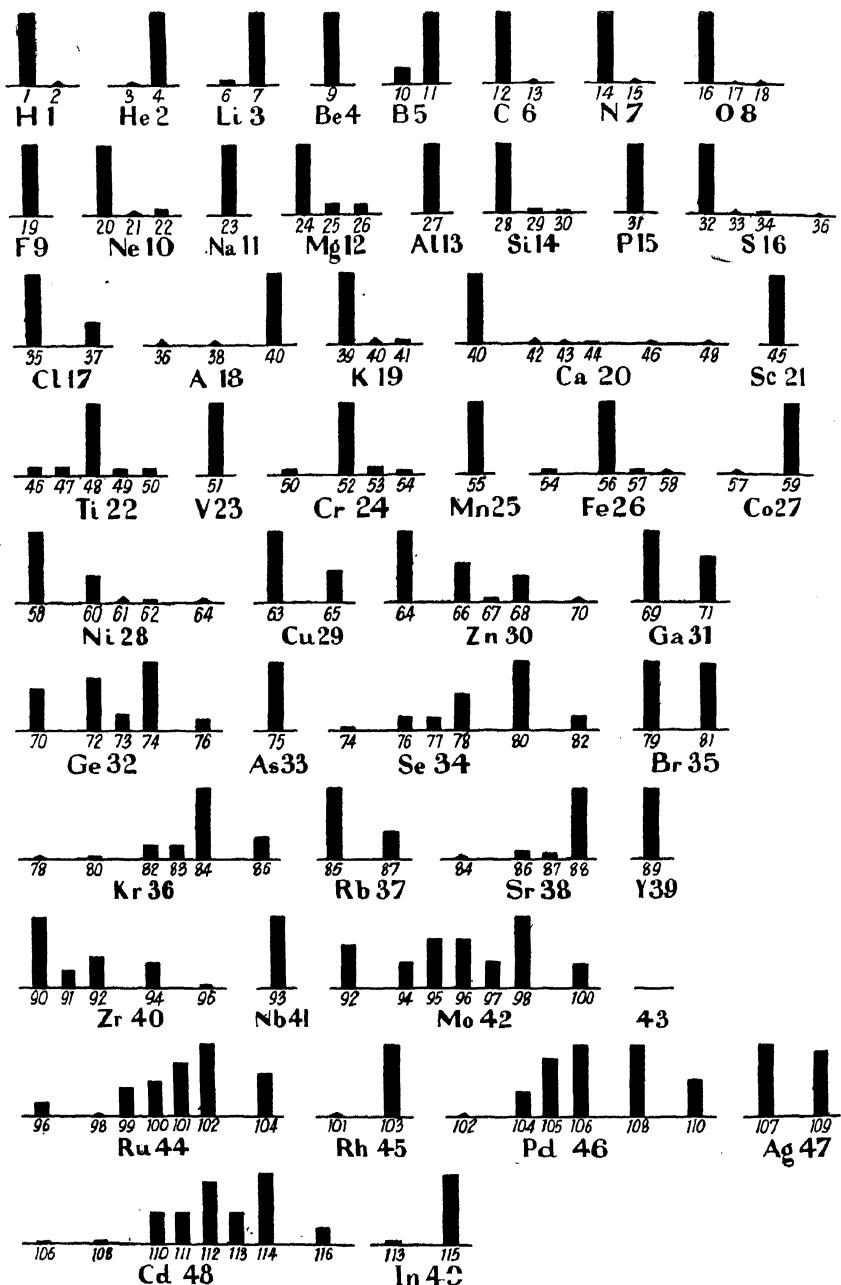


FIG. 40.—Isotopes of Elements of Atomic Number 1-49.

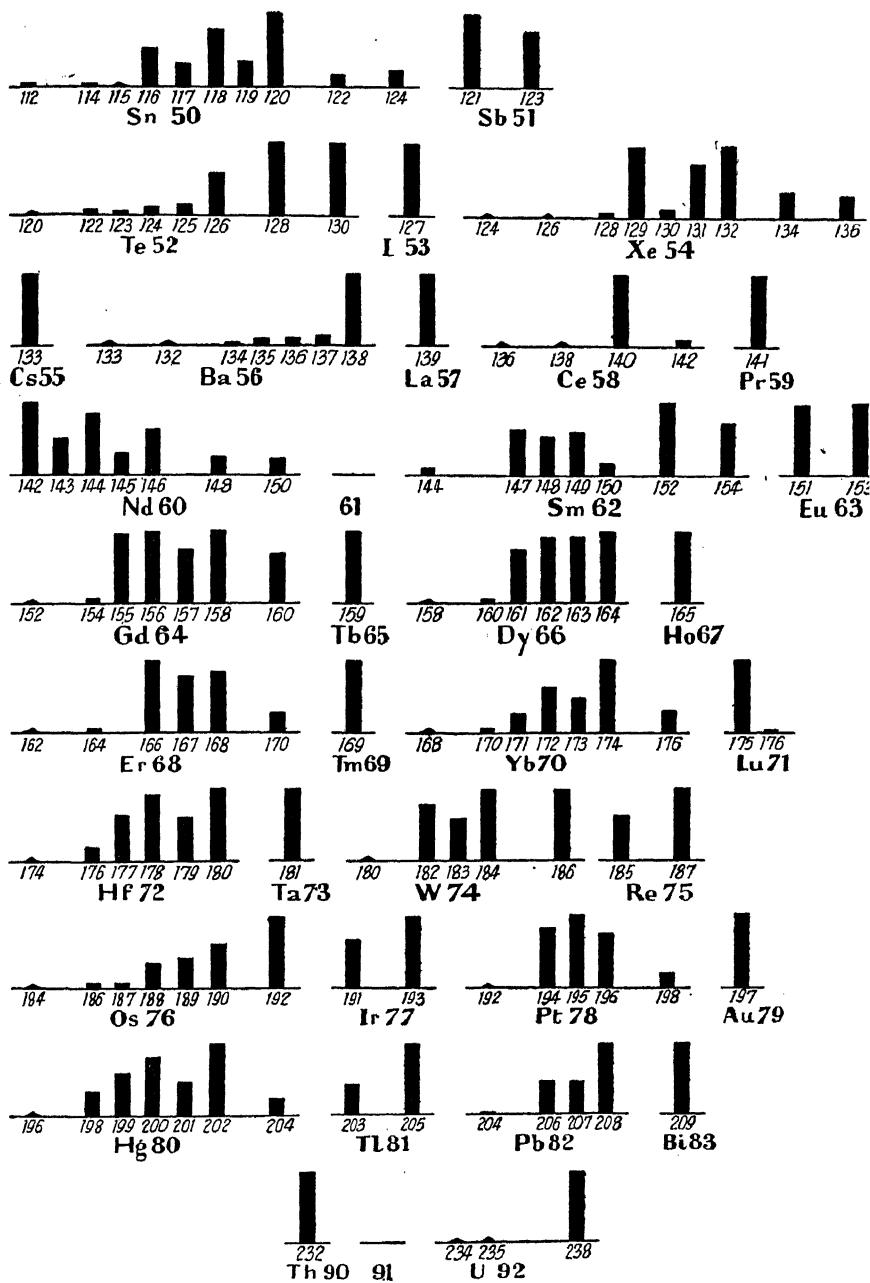


FIG. 41.—Isotopes of Elements of Atomic Number 50–92.

complex elements, and, with the possible and numerically insignificant exception of boron, all had given consistently negative results. This conclusion has been in general supported by the later more accurate work with the mass spectrometer. We may therefore say briefly that whereas it is impossible to obtain a mixture of elements which we may regard as a fair sample of cosmic matter it is very nearly as impossible to obtain a mixture of isotopes which is *not* a fair sample of a complex element.

There was therefore a slight hope that systematic measurement of these ratios might reveal relations of fundamental interest. On this account, and also incidentally to check chemical atomic weights by purely physical methods, the problem was attacked by the methods of mass spectrum photometry.<sup>1</sup>

At the outset the results seemed promising. The very close equality of <sup>79</sup>Br, <sup>80</sup>Br and of <sup>82</sup>Kr, <sup>83</sup>Kr might have significance, and other similarities of ratio were noticed, but as results accumulated the hope was seen to be unfounded, and an analysis of the first 250 ratios showed no closer groupings than would be expected from pure chance.

These results together with the more accurate ones obtained with mass spectrometers have already been given for each individual element in Part III and will be found tabulated in Appendix I. They are reproduced in a graphical manner in Figs. 40 and 41. Here the heights of the columns indicate the proportion of each isotope present, the most abundant one being represented as a fixed height as a standard of comparison. Abundance of less than 2 per cent. of the standard is too small for this form of representation and the occurrence of rare isotopes is indicated by triangles. The height of these has little significance except to indicate which of two mass numbers is the more abundant in the same element.

In such a form of nuclear periodic table the eye cannot fail to note many interesting and suggestive facts such as the very marked contrast between argon and calcium. There is clearly a family likeness between many of the more complex groups, the abundance growing towards the median mass numbers and then fading away again. In contrast there are the groups of zinc, zirconium and neodymium with the lightest isotope the most abundant on the one hand, and on the other the remarkable rarity of the lighter isotopes of tellurium and barium. The importance of the differences 44 and 88, already mentioned in connection with mass numbers, is brought out in a most remarkable manner by the series of clusters magnesium, zinc, cadmium and mercury, and only a little less so in silicon, ger-

<sup>1</sup> V. p. 86.

manium, tin and lead. There is also a striking resemblance between such groups as cadmium, tin, hafnium and mercury.

**120. Isotopic moment and separability.**—In addition to information on mean atomic weights other useful data on complex elements can be calculated from the relative abundance of their isotopes.

The relative importance of an isotope in shifting the mean mass number is clearly the product (abundance)  $\times$  (distance from the mean mass number on the mass scale). The sum of such products for all the isotopes is a constant, of considerable interest, which may be termed the "isotopic moment" of an element. It will clearly be 0 for a simple element and 1 for a complex element (such as bromine), which consists of two equally abundant isotopes two units apart. This number is not only roughly proportional to the error to be expected in an atomic weight calculated from the mass spectrum, but is an accurate measure of the ease with which the atomic weight may be altered, per unit, artificially by such methods as diffusion or free evaporation. In the case of one complex element, mercury, the isotopic moment has been evaluated experimentally in the latter way<sup>1</sup> and found to be identical with that later determined by the photometry of its mass spectrum.

If the isotopic moment of an element is divided by its mean atomic weight another constant which may be termed "separability" is obtained. This is a measure of the *percentage* change in atomic weight to be expected from such methods of separation.

Table XIV gives a list of a number of typical complex elements arranged in order of their isotopic moment and in order of their separability. The position of boron at the head of the latter supplies the reason for it being the only element so far found to show definite indications of variability in chemical atomic weight in Nature.

TABLE XIV

Isotopic Moments.				Separabilities $\times 100$ .			
Mo . . .	1.87	Ni . . .	0.94	B . . .	3.01	Br . . .	1.25
Sn . . .	1.77	Kr . . .	0.87	Zn . . .	2.16	Kr . . .	1.04
Te . . .	1.74	Pb . . .	0.84	Cl . . .	2.04	Rb . . .	0.91
Xe . . .	1.71	Tl . . .	0.83	Ge . . .	2.03	Sb . . .	0.79
Se . . .	1.49	Rb . . .	0.79	Mo . . .	1.95	Os . . .	0.73
Ge . . .	1.48	Cl . . .	0.72	Se . . .	1.89	Hg . . .	0.70
Zn . . .	1.41	Ne . . .	0.36	Ne . . .	1.78	W . . .	0.67
Hg . . .	1.40	B . . .	0.32	Li . . .	1.73	H . . .	0.6
Os . . .	1.40	Cr . . .	0.31	Ni . . .	1.60	Cr . . .	0.60
W . . .	1.23	K . . .	0.19	Sn . . .	1.49	K . . .	0.49
Br . . .	1.00	Li . . .	0.12	Te . . .	1.37	Pb . . .	0.41
Sb . . .	0.96	H . . .	0.006	Xe . . .	1.30	Tl . . .	0.40

<sup>1</sup> V. p. 254.

**121. The constancy of chemical atomic weights.**—One of the first difficulties in the way of accepting the idea of the complex constitution of an element such as chlorine was the constancy of its atomic weight. This had been determined by many different observers using different methods and the results were always the same within a very small experimental error. This difficulty was met, in the first place, by the argument that the vast majority, if not all, of the really accurate values were obtained from chlorine which must have been originally derived from the sea. The sea has been mixed for so long that it would be absurd to expect to find chlorines of different chemical atomic weights in it. Had ordinary galena been the only source of lead used in the atomic weight determinations given on page 16 no difference would have been found. It was only by examining the lead from extraordinarily radioactive sources that the results were obtained which gave such definite and valuable support to the theory of isotopes.

The atomic weight of chlorine from sources other than the sea soon received the attention of chemists, though it is naturally very difficult to be at all sure that any known source of chlorine is not of marine origin. Mlle Irene Curie<sup>1</sup> examined the atomic weight of chlorine from three minerals whose marine origin seems unlikely. The values obtained from a sample of sodalite (sodium aluminium chlorosilicate) from Canada, and from a sample of calcium chlorophosphate from Norway agree with the value for chlorine from seawater. The value 35.60, for chlorine from a sample of sodium chloride from a desert region in Central Africa was slightly high.

Later very careful investigations were made by Mlle Ellen Gleditsch and B. Samdahl<sup>2</sup> on chlorine in an apatite from Oodegaarden in Bamle, Norway. This mineral is found in lodes and the investigators were confident that it was formed from the primary magma and had never been in contact with water. Atomic weight determinations showed no difference between this chlorine and that from ordinary sources. In further confirmation Margot Dorenfeldt<sup>3</sup> compared the specific gravities of saturated solutions of sodium chloride made from the apatite material with similar solutions of the ordinary salt. When all corrections had been made, the ordinary chloride gave a figure 1.202867 as compared with 1.202855 for the apatite chloride. The quantity of dry sodium chloride from equal volumes of the solutions was 3.31262 for ordinary, and 3.31267 for the Bamle sample. The differences are insignificant. Later chlorine was again examined by

<sup>1</sup> I. Curie, *Compt. Rend.*, **172**, 1025, 1921.

<sup>2</sup> Gleditsch and Samdahl, *ibid.*, **174**, 746, 1922.

<sup>3</sup> Dorenfeldt, *J. Amer. Chem. Soc.*, **45**, 1577, 1923.

Gleditsch,<sup>1</sup> Harkins and Stone,<sup>2</sup> and Menzies,<sup>3</sup> but although very wide ranges of terrestrial and meteoric sources were used no variation was detected.

The comparison of the atomic weights of elements from meteorites with those of terrestrial ones is of particular interest in this connection. The first work of this kind was done on iron by Baxter and Thorvaldson<sup>4</sup> before the discovery of isotopes. No difference in atomic weight was detected.

A comparison of the atomic weights of terrestrial and meteoric nickel made by Baxter and Parsons,<sup>5</sup> whilst three experiments with meteoric nickel gave 58.68, as a mean of nine determinations with the terrestrial material the figure 58.70 was found. The standard value found by Richards and Cushman was 58.68. The difference found between terrestrial and meteoric nickel was considered to be within the limits of experimental error. On repeating this work with the aid of the most refined methods Baxter and Hilton<sup>6</sup> found identically the same value 58.70 for meteoric and terrestrial nickel.

Boron, which has the highest constant of separability, is the only element which has given fairly well substantiated evidence of variation in nature. Although Munro<sup>7</sup> could detect none Briscoe and others<sup>8</sup> have reported variations detected both by atomic weight determinations and also by density measurements. The figures are not large; their later report indicates a real difference of about 0.01 of a unit in the mean atomic weight of boron from California and from Asia Minor.

A most important and conclusive paper on the subject is that of Jaeger and Dijkstra.<sup>9</sup> They worked on the element silicon, which has as wide a distribution in Nature as any complex element, and examined it by determining the density of tetraethylsilicane made from it by the Grignard reaction. After carrying out this operation with silicones from six different cosmic and six different terrestrial sources, they found no difference of density greater than 0.0006 per cent. By further investigation they were able to show conclusively that even these small differences were to be attributed to the presence

<sup>1</sup> Gleditsch, *J. Chim. Physique*, **21**, 456, 1924.

<sup>2</sup> Harkins and Stone, *Proc. Nat. Acad. Sci.*, **11**, 643, 1925; *J. Amer. Chem. Soc.*, **48**, 938, 1926.

<sup>3</sup> Menzies, *Nature*, **116**, 643, 1925.

<sup>4</sup> Baxter and Thorvaldson, *J. Amer. Chem. Soc.*, **33**, 337, 1911.

<sup>5</sup> Baxter and Parsons, *ibid.*, **43**, 507, 1921.

<sup>6</sup> Baxter and Hilton, *ibid.*, **45**, 694, 1923.

<sup>7</sup> Munro, *Trans. Chem. Soc.*, **121**, 986, 1922.

<sup>8</sup> Briscoe, *J. Chem. Soc.*, **127**, 696, 1925; **282**, 1927.

<sup>9</sup> Jaeger and Dijkstra, *Zeit. Anorg. Chem.*, **143**, 233, 1925.

of traces of by-products too small to be detected chemically. They conclude that terrestrial and meteoric silicon give products not differing by more than the error of experiment which was 0·00004 per cent.

Work on other elements, mercury,<sup>1</sup> antimony,<sup>2</sup> copper,<sup>3</sup> and nitrogen,<sup>4</sup> failed to show measurable variations.

When direct and accurate comparisons of the abundances of isotopes by mass spectrometers became available variations were discovered in the constitution of some elements, such as potassium and carbon, which have already been noted in Part III, but these, when expressed as changes in chemical atomic weight, only amount, at the most, to a few parts in ten thousand.

The latest research bearing on the question is that of Valley and Anderson,<sup>5</sup> who have compared electrometrically the ratios of abundance of the isotopes of terrestrial and meteoric iron with the following results :

Mass number	.	54	56	57	58
Terrestrial	.	6·37	100	2·37	0·34
Meteoric	.	6·32	100	2·32	0·33

such remarkable constancy, considering the origin of the samples, is very impressive.

It seems reasonably safe to conclude that although, owing to the variation in its constitution, the expression of the chemical atomic weight of oxygen itself beyond a certain accuracy is meaningless,<sup>6</sup> yet, so long as artificial means of separation are not resorted to, the atomic weights of normal naturally occurring elements are constant enough for all the ordinary operations of chemistry.

**122. The agreement between chemical and physical atomic weights.**—The development of methods of measurement of the masses and relative abundance of isotopes enabled chemical atomic weights to be checked for the first time by purely physical means. The atomic weights deduced from determinations of the densities of gases are of course to be included among the chemical ones, for they depend on processes of purification which are essentially chemical.

The early results with the first mass spectrograph were in agreement with those already obtained by chemical methods. Not only did the masses of oxygen, carbon, helium and nitrogen, assumed to be simple elements, agree with accepted values, but the isotopes of

<sup>1</sup> Brönsted and Hevesy, *Nature*, **109**, 813, 1922.

<sup>2</sup> McAlpine, *J. Amer. Chem. Soc.*, **51**, 1745, 1929.

<sup>3</sup> Phillips, *ibid.*, 400, 1929.

<sup>4</sup> Cady and Beecher, *Science*, **68**, 594, 1928.

<sup>5</sup> *Phys. Rev.*, **59**, 113, 1941.

<sup>6</sup> Urey and Greiff, *J. Amer. Chem. Soc.*, **57**, 321, 1935.

the complex elements neon, chlorine and argon were found to obey the "whole-number rule" and, from a rough estimate of the relative intensity of their lines, appeared to be present in the proportion expected from their chemical atomic weights. Of still greater interest was the discovery that the mass of the hydrogen atom when compared with helium and oxygen was not a whole number but corresponded with the well-established chemical value 1.008.

The first serious discrepancy was noted in the case of krypton, which gave a group of six lines corresponding to masses definitely integral, but when the position of the centre of gravity of this group was estimated it gave a value for the mean atomic weight of  $83.5 \pm 0.3$ . The accepted International figure deduced from the density was 82.92. On the other hand, the relative intensities of the boron lines 10 and 11 suggested a value less than the chemical one, 10.90, then in use. Xenon when analysed gave an estimated mean weight  $131.3 \pm 0.3$  (Intl. 130.2), showing a discrepancy similar to that of krypton. The most glaring case was antimony, which gave two lines of almost equal strength 121, 123, whereas the chemical value 120.2 was still in use. The chemical figure 9.1 for beryllium was not in agreement with the positive ray evidence that this was essentially a simple element. Revision of the chemical atomic weights reduced to small values the discrepancies in the cases of boron, beryllium and antimony, but those of krypton and xenon remained.

In all these cases the relative abundance of the isotopes was estimated visually from the appearance of the lines on their mass spectra. The first actual measurements of relative abundances were made by Dempster who, by assuming the whole-number rule, was able to show that the isotopic constitutions of magnesium, potassium, calcium and zinc were in fair accord with their chemical atomic weights.

The construction of the second mass spectrograph and the development of methods of photometry brought the accuracy of the physical method up to 1 or 2 parts in 10,000, a precision comparable with the best chemical practice. About the same time the discovery of the complexity of oxygen revealed that the scales used were not identical. The discrepancies between the physical and chemical values were discussed by the writer in the 1932 Liversidge Lecture<sup>1</sup> and the need for further work on both methods emphasized. At that time Bainbridge had explained the discrepancy of tellurium and those of krypton and xenon were much reduced by revision of their densities. Selenium was brought into accord by chemical revision and the mass spectrum evidence that niobium and tantalum were simple was con-

<sup>1</sup> Aston, *J. Chem. Soc.*, 2888, 1932.

firmed by the chemical work of Honigschmid. The simplicity of phosphorus and its negative packing fraction were demonstrated in 1927, but the chemical value was well established, and it was not till ten years later that the discrepancy, in this case not a large one, was also removed by the work of Honigschmid.

The very interesting cases of hydrogen, erbium and osmium have been fully commented on in Part III and those of caesium, neodymium and gadolinium noted. The serious discrepancies which remain are indicated in Table XV.

TABLE XV

Element.	Atomic Number.	1940 Intl. At. Wt.	Physical At. Wt.	Percentage Difference.
Sc	21	45.10	44.96	+ 0.31
Kr	36	83.7	83.817	- 0.14
Ru	44	(101.7)	101.1	+ 0.6
Pd	46	106.7	106.55	+ 0.15
Sm	62	150.43	150.1	+ 0.22
Tb	65	159.2	158.94	+ 0.16
Tm	69	169.4	168.92	+ 0.28
Ir	77	193.1	192.21	+ 0.46
Au	79	197.2	196.98	+ 0.12

There are differences of the same order for Er, Yb and Hf but they are not significant as the relative abundances of their isotopes are not known with sufficient certainty. In the case of Ru a new chemical value, agreeing with mass spectra, has recently been published but not yet adopted.

In conclusion there can be no doubt that the discovery of isotopes has had a most profound effect upon the philosophical significance of chemical atomic weight determinations. Though many will agree that Soddy's bitter comment on the nineteenth-century chemists : "Their hard-won results, for the moment at least, appear as of little interest and significance as the determination of the average weight of a collection of bottles, some of them full and some of them more or less empty,"<sup>1</sup> is too pessimistic, it is nevertheless true that were the vast mass of chemical data lost, the Table of Atomic Weights could be reconstructed to-day, entirely from mass spectrum evidence, as complete and, with the possible single exception of the element copper, as accurate.

**123. The meaning of the word "element."**—The exact idea conveyed by the word "element" in chemistry and physics has given rise to endless difficulties in the past. In this connection Crookes in 1886 sums up the matter as follows : "Of the attempts hitherto made to define or explain an element, none satisfy the demands of the

<sup>1</sup> Soddy, *The Interpretation of the Atom*, p. 50, 1932.

human intellect. The textbooks tell us that an element is 'a body which has not been decomposed'; that it is 'a something to which we can add, but from which we can take away nothing,' or 'a body which increases in weight with every chemical change.' Such definitions are doubly unsatisfactory: they are provisional, and may cease to-morrow to be applicable to any given case. They take their stand, not on any attribute of things to be defined, but on the limitations of human power; they are confessions of intellectual impotence."

There was good reason for this dissatisfaction. The discovery ten years later of the electron, and the subsequent electrical theory of matter robbed the word of any pretence to its original meaning; for although Ramsay attempted to introduce into chemistry electricity itself as an element, it soon became obvious that this extension was unsuitable. The discovery of isotopes brought us face to face with two possible alternatives. The first was to call each isotope, as it was discovered, a new element. This had serious objections. A new word would be necessary to express such substances as chlorine or magnesium, hitherto called elements, and also the word element would mean something entirely different from what it had meant in all the chemical and physical literature of the past century. It would moreover be still subject to alterations in the future. The second was to fix the word precisely, now and for the future, as meaning a substance with definite chemical and spectroscopic properties which may or may not be a mixture of isotopes—in other words, to associate it exclusively with the conception of atomic number.

The second alternative has now been generally adopted.

## CHAPTER XIV

### ISOTOPE EFFECT IN MOLECULAR SPECTRA

As has already been described,<sup>1</sup> the early optical experiments showed no detectable spectral differences in such isotopes as thorium and ionium. Later work with higher accuracy showed small differences in the line spectra<sup>2</sup> and much larger ones in the band spectra of isotopes. The theory of the "isotope effects" has now been so completely developed by means of quantum mechanics that observation of optical spectra has become a valuable addition to that of mass spectra in the investigation of the isotopic constitution of elements. By its means exceedingly important discoveries of rare isotopes have been made and it can also be used to measure relative masses and abundances, and to give information upon the nuclei of isotopes which is proving of the first importance in modern nuclear theory.

The isotope effect is far more clearly marked in molecular spectra than in atomic, as well as being much simpler in principle. Accordingly it seems preferable to deal first with the results from the analysis of molecular bands of diatomic molecules.

**124. The vibrational effect.**—The nuclei of any diatomic molecule can vibrate along the inter-nuclear axis. When the two nuclei are different, as for example in HCl or CO, the vibrations will cause a change of electric moment of the molecule, which will show itself spectroscopically in *vibrational bands* (molecules such as H<sub>2</sub> or N<sub>2</sub>, which are completely symmetrical and without any electric moment either at rest or when vibrating, obviously cannot have vibrational bands). The molecule can also rotate about a line perpendicular to the inter-nuclear axis ; the quantum corresponding to this movement will be very much smaller than the vibrational quantum, and so every change in vibration will be accompanied by a number of changes in rotation. Thus if we write

$$E_{\text{vib. rot.}} = E_{\text{vib.}}(v) + E_{\text{rot.}}(J)$$

for the energy of a vibrating-rotating diatomic molecule, there will

<sup>1</sup> V. p. 9.

<sup>2</sup> Aronberg, *Proc. Nat. Acad. Sci.*, **3**, 710, 1917 ; Merton, *Proc. Roy. Soc., A*, **96**, 388, 1920.

be many possible changes in  $J$  (the rotational quantum number) for one change in  $v$  (the vibrational quantum number). This is, of course, the explanation of the well-known rotational structure of vibrational bands. For instance, we may take the normal case of absorption, in which the molecule in the lower state has no vibrational quanta ( $v'' = 0$ ; we neglect half-quantum numbers for the moment) and is raised to an upper state<sup>1</sup> where  $v' = 1$ . During this transition the various  $J''$ 's associated with  $v'' = 0$  (for the molecule will be rotating, though not vibrating, in the ground state) will change both positively and negatively. Some of the  $J''$ 's will gain in quantum number and some lose. In this way we arrive at the typical vibration-rotation band, in which for a single change in vibration such as ( $v'' = 0 \rightarrow v' = 1$ ) we have a number of rotational lines

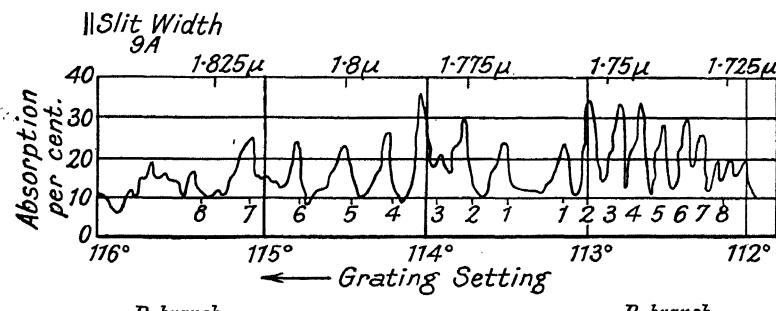


FIG. 42.—(2,0) Band of HCl under fairly low dispersion.  
The isotope effect is indicated, but the component lines are not resolved.

corresponding to an increase of  $J$  ( $J'' < J'$ ) which form an approximately evenly spaced sequence of lines, the so-called R branch, and a similar number of lines in which  $J'' > J'$ , the so-called P branch. The arrangement is illustrated in Fig. 42.

If we now consider the energy of vibration only, the way in which an isotope effect will appear in the band spectrum is very easy to see. The energy of vibration will be expressed in the usual way as

$$E_{vib/hc} = E(v) = \omega_e(v + \frac{1}{2}) - x_e\omega_e(v + \frac{1}{2})^2 + \dots \quad (1)$$

The vibrational quantum number  $v$  takes the values 0, 1, 2, 3 . . . ,  $\omega_e$  is the frequency of vibrations of very small amplitude and  $x_e$  . . . are small constants which describe the anharmonic nature of the vibrations of the nuclei.

Changes from  $E''(v)$  to  $E'(v)$  are permitted in which  $v'$  and  $v''$

<sup>1</sup> In conformity with the established practice, the *upper* state in an energy transition, whether of emission or absorption, is denoted by single point ('), and the *lower* state by double point (").

have any value. It is clear that a change from  $v'' = 0 \rightarrow v' = 1$  will give a frequency very close to  $\omega_e$  since neglecting  $x_e \dots$

$$E(v') - E(v'') = \omega_e [v' + \frac{1}{2}] - [v'' + \frac{1}{2}] \dots \quad . \quad . \quad . \quad (2)$$

Thus the position of the observed vibrational band will give a close correspondence to the actual frequency of the nuclear vibration. The order of magnitude of the nuclear vibration shows at once that the vibrational bands ( $v'' = 0 \rightarrow v' = 1$ ) will be found between 1000 and  $4000 \text{ cm}^{-1}$ , for light molecules ; this range is in the near infrared, where all vibrational-rotational bands are actually observed.

The value of  $\omega_e$ , the frequency of vibration of the nuclei, depends on their *reduced mass*  $\mu$ , given by  $m_1 m_2 / m_1 + m_2$  where  $m_1$  and  $m_2$  are the nuclear masses, and the force between them. From the simplest of considerations, we can assert that for given forces

$$\omega_e \propto \mu^{-\frac{1}{2}}.$$

The vibrational isotope effect is at once obvious. For, assuming what is theoretically reasonable and experimentally completely proved, that the force fields in two isotopic molecules such as  $\text{H}^{35}\text{Cl}$  and  $\text{H}^{37}\text{Cl}$  are identical, we have

$$\frac{\omega_{eI}}{\omega_{eII}} = \frac{\mu_I^{-\frac{1}{2}}}{\mu_{II}^{-\frac{1}{2}}}.$$

From (i) and (ii) the value of  $\omega_e$  determines the position of the vibrational bands : and if  $\nu_{eI}$  is the wave number of the vibrational band of the molecular isotope I, which vibrates with a frequency of  $\omega_{eI}$ , then the corresponding band for the molecular isotope II, which vibrates with a frequency of  $\omega_{eII}$ , will be displaced by an amount which can be calculated from

$$\frac{\nu_{eI}}{\nu_{eII}} = \frac{\mu_I^{-\frac{1}{2}}}{\mu_{II}^{-\frac{1}{2}}}.$$

The quantity  $\frac{\nu_{eI}}{\nu_{eII}}$  is usually called  $\rho$ .

We should expect that the molecule  $\text{H}^{37}\text{Cl}$ , vibrating by reason of its increased mass a little slower than  $\text{H}^{35}\text{Cl}$ , would have its vibrational band displaced towards smaller frequencies. The displacement can be calculated from the  $\rho$  for the two molecules and the position of the vibrational band of  $\text{H}^{35}\text{Cl}$  ; it comes out as approximately  $2 \text{ cm}^{-1}$ .

This *vibrational isotope effect* clearly applies equally to all the rotational lines of a vibration-rotation band ; in the vibrational spectra of HCl these considerations predict that on the low frequency side of each rotational line of  $\text{H}^{35}\text{Cl}$  there should be a less intense satellite due to  $\text{H}^{37}\text{Cl}$ , about  $2 \text{ cm}^{-1}$  away. Experiment shows at once that

the vibrational isotope exists in the way sketched out. In 1919 Imes<sup>1</sup> resolved the HCl vibration-rotation bands corresponding to vibrational changes from  $0 \rightarrow 1$  and  $0 \rightarrow 2$ . This investigation marks the beginning of the detailed study of vibrational-rotational spectra; there are now few simple molecules whose vibration-rotations have not been studied in detail.

In the (2,0) band<sup>2</sup> Imes commented on the experimental fact that the rotational components were broadened on the side of small frequencies (see Fig. 42). The dispersion he used was comparatively low, and lines separated by  $4 \text{ cm}^{-1}$  or so could not be sharply resolved. The explanation of this effect was given independently by Loomis<sup>3</sup> and Kratzer<sup>4</sup> in 1920; they interpreted it as the vibrational isotope effect which has just been described. The approximate separation of the  $\text{H}^{35}\text{Cl}$  and  $\text{H}^{37}\text{Cl}$  components was taken as  $4.5 \text{ cm}^{-1}$ , in good agreement with  $(\rho - 1)\nu_e$  for the (2,0) band of HCl.

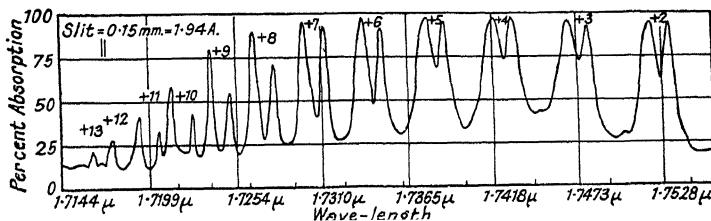


FIG. 43.—The R branch of the (2,0) band of HCl under highest dispersion yet reached in the infra-red.

The isotope components are resolved; there is no sign of  $\text{H}^{37}\text{Cl}$  (Hardy and Sutherland). Cf. Fig. 42. It should be noted that the direction of increasing wave-length is different in the two diagrams.

The general outline of the explanation was obviously sound. In fact, most of the important results derived from the isotope effect in molecular spectra are due to the simple principle of the alteration in frequency produced by an isotopic difference in  $\mu$ . [It should be emphasized that this effect is purely *vibrational*; each rotational line in the vibration-rotation band consists of a term  $\nu_e + \nu'$  and we are here considering only the displacement of  $\nu_e$ .]

Since Imes's work there have been immense improvements in experimental technique in the infra-red. It is now possible to resolve

<sup>1</sup> Imes, *Astrophys. J.*, 50, 251, 1919.

<sup>2</sup> Throughout these chapters the nomenclature suggested and adopted by Mulliken is used. (2,0) means

$\nu'$  upper state = 2;  $\nu''$  lower state = 0.

<sup>3</sup> Loomis, *Astrophys. J.*, 52, 248, 1920.

<sup>4</sup> Kratzer, *Zeits. Phys.*, 3, 460, 1920.

completely the isotopic components of the (2,0) band of HCl and measure their positions with great accuracy. The most precise research, which must be something like the ultimate expression of the experimental facts, has been carried out by Hardy and Sutherland,<sup>1</sup> using Hardy's<sup>2</sup> infra-red spectrometer. Fig. 43 shows how clear-cut their results are. The lines of the H<sup>35</sup>Cl and H<sup>37</sup>Cl molecules are widely separated (compare Fig. 42) and the difference between them—the ( $\rho - 1$ ) $\nu_e$ —can be accurately measured. The isotopic differences for lines of the R branch are as follows :

TABLE XVI  
ISOTOPE SEPARATIONS IN (2,0) BAND OF HCl—POSITIVE BRANCH

J (number of line)	Separation in cm <sup>-1</sup>
2	4·04
3	4·03
4	4·03
5	4·21
6	4·21
7	4·14
8	4·24

From the theory of the vibrational isotope effect the differences should be exactly the same (as each line in the H<sup>37</sup>Cl band corresponds to the *same* vibration ( $0 \rightarrow 2$ ) and will have the same ( $\rho - 1$ ) $\nu_e$ ). They are very nearly the same ; and the vibrational effect is obviously the chief source of the displacement. But the accuracy of the experimental method is enough to give significance to the gradual increase from 4·04 to 4·24 with increasing values of J. This secondary effect is quite distinct from the vibrational displacement, and to understand it we must look a little more closely into the energy states of a vibrating-rotating molecule.

**125. The rotational isotope effect.**—The energy of a vibrating-rotating molecule can be represented approximately by

$$E(v) + E(r) = \omega_e(v + \frac{1}{2}) + x_e\omega_e(v + \frac{1}{2})^2 \dots$$

$$+ \frac{\hbar J}{8\pi^2 I} \cdot (J + 1) + XJ^2(J^2 + 1) \dots \quad (3)$$

where I is the moment of inertia and is expressed by  $\mu r_o$ ,  $r_o$  being the distance between the nuclei at rest. X . . . are small constants involving I. Each side of the equation has been divided by  $\hbar$ .

The isotopic alteration due to the vibrational terms  $\omega_e(v + \frac{1}{2})$ ,  $x_e\omega_e(v + \frac{1}{2})^2 \dots$  has already been discussed ; the rotational terms

<sup>1</sup> Hardy and Sutherland, *Phys. Rev.*, **41**, 471, 1932.

<sup>2</sup> Hardy, *ibid.*, **38**, 2162, 1931.

$\hbar J$ 

$+ 1)$ ,  $XJ^2(J + 1) \dots$  have, however, been omitted up to now.

The inter-nuclear distance  $r_o$  will vary very little in isotopic vibrations, from, say,  $H^{35}Cl$  to  $H^{37}Cl$ , and changes in I due to changes in  $r_o$  will be quite negligible. But  $\mu$  will, of course, vary and I and the rotational terms will consequently differ for isotopic molecules, for  $H^{35}Cl$  and  $H^{37}Cl$ , for instance. There will therefore be a rotational displacement in the vibrational-rotational bands: a glance at the energy expressions shows that it will be represented approximately by

$$\frac{\nu_{rII}}{\nu_{rI}} = \rho^2 \text{ (for } \mu, \text{ and not } \mu^{-\frac{1}{2}}, \text{ enters into the rotational terms)}$$

and the displacement becomes:  $\nu_{rII} - \nu_{rI} = (\rho^2 - 1)\nu_{rI}$ . Since  $\nu_{rI}$  (which expresses the change in rotational energy from  $J'' \rightarrow J'$ , for a given vibrational change) is much smaller than  $\nu_e$ , this displacement will be much less than the vibrational, even though the factor in  $\rho$  is larger. For a single change in vibration, there will be many  $\nu_r$ 's of values increasing with the rotational quantum number: accordingly the rotational displacement will get larger with increasing  $J$ . And so, added to the constant vibrational displacement, we have the small rotational displacement which becomes greater with increasing quantum number. The combination of these two effects is shown very beautifully by the results of Hardy and Sutherland.

**126. Accurate theory of the vibrational and rotational isotope effects in vibration-rotation bands.**—Almost all the general features of the isotope effect in molecular spectra can be understood from the two approximate relations which have been dealt with:

$$\nu_{eII} - \nu_{eI} = (\rho - 1)\nu_{eI} \text{ vibrational displacement}$$

$$\nu_{rII} - \nu_{rI} = (\rho^2 - 1)\nu_{rI} \text{ rotational displacement}$$

where  $\nu_r \ll \nu_e$  (for  $HCl$ ,  $\nu_e$  is about 200 times as great as  $\nu_r$ ) and  $\rho$  is a little larger than 1.

The accurate theory of these effects is only necessary to explain the minute deviations from these simple rules. It is derived from the complete energy expression for a vibrating rotating molecule, derived by Fues<sup>1</sup> from quantum mechanical considerations:

$$\begin{aligned} E = A + \hbar\omega_e(v + \frac{1}{2})[1 + P(J + \frac{1}{2})^2] \\ + \frac{\hbar^2}{8\pi^2 I}(J + \frac{1}{2})^2[1 - K^2(J + \frac{1}{2})^2] \\ - \frac{\hbar^2}{8\pi^2 I}(v + \frac{1}{2})^2 Q \quad \dots \dots \dots \dots \end{aligned} \quad (4)$$

<sup>1</sup> Fues, *Ann. Physik.*, **80**, 367, 1926.

when  $K = \frac{\hbar}{4\pi^2\omega_e I}$ ,

$$P = \frac{3}{2}K^2(1 + 2Q_3),$$

$$Q = 3 + 15Q_3 + \left(\frac{15}{2}\right)Q_3^2 + 3Q_4$$

$Q_3$  and  $Q_4$  are constants in the potential energy expressions which measure the anharmonicity of the vibration.

From this we get an expression for the frequencies in any vibration-rotation bands corresponding to a change in  $v$  of  $\Delta v$

$$\begin{aligned} \nu &= \omega_e \Delta v + \frac{1}{2} \omega_e P \Delta v - \frac{\hbar}{8\pi^2 I} Q (\Delta v^2 + \Delta v) \\ &\quad - J \left( -\omega_e P - \omega_e P \Delta v + \frac{\hbar}{4\pi^2 I} - \frac{\hbar K^2}{8\pi^2 I} \right) \\ &\quad - J^2 \omega_e P \Delta v - J^3 \left( \frac{\hbar}{8\pi^2 I} \right) 4K^2. \end{aligned}$$

In this formula  $J$  positive gives the lines of the R branch,  $J$  negative the P branch. Terms in  $\frac{\hbar^2 K^2}{8\pi^2 I}$  have been shown by Colby<sup>1</sup> to be negligible.

The difference between the frequencies of molecular isotopes will be (the vibrational and rotational terms both enter, of course, into this expression)

$$\begin{aligned} \nu_I - \nu_{II} &= 1 - \rho \left[ (\omega_e \Delta v - \frac{1}{2} \omega_e P \Delta v (1 + \rho + \rho^2) - \frac{\hbar Q (\Delta v^2 + \Delta v)}{8\pi^2 I}) \right. \\ &\quad \left. + J (-\omega_e P (1 + \Delta v) (1 + \rho + \rho^2) + \frac{\hbar}{4\pi^2 I} (1 + \rho) \right. \\ &\quad \left. - J^2 \omega_e P \Delta v (1 + \rho + \rho^2)). \right. \end{aligned}$$

Putting  $\rho = 1$  except in the first factor

$$\begin{aligned} \nu_I - \nu_{II} &= 1 - \rho \left[ \nu_c - \frac{\hbar}{8\pi^2 I} Q (\Delta v^2 + \Delta v) - \frac{1}{2} \omega_e P \Delta v \right] \\ &\quad + J \left[ \frac{\hbar}{h\pi^2 I} - 3P\omega_e (1 + \Delta v) \right] - 3J^2 P \omega_e \Delta v \end{aligned}$$

when  $\nu_c = \omega_e \Delta v - \frac{1}{2} \omega_e P \Delta v - \frac{\hbar}{8\pi^2 I} Q (\Delta v^2 + \Delta v)$

and  $\nu_c$  is the wave number of the centre of the band.

The agreement of the accurate theory with the most precise

<sup>1</sup> Colby, *Phys. Rev.*, 34, 53, 1929.

measurements in vibration-rotation bands is shown in Table XVII, and in Table XVI, p. 222, which gives the data of Hardy and Sutherland.

TABLE XVII  
ISOTOPE SEPARATIONS IN THE HARMONIC BAND—POSITIVE BRANCH

<i>j</i>	Calculated.		Observed.					
	(cm <sup>-1</sup> ).	(A).	Hardy and Sutherland.		Hettner and Böhme. <sup>1</sup>		Meyer and Levin. <sup>2</sup> (cm <sup>-1</sup> ).	
			(cm <sup>-1</sup> ).	(A).	(A).	(A).		
2	4.08	12.5	4.04	12.3	12.5	12.5	4.20	
3	4.10	12.5	4.03	12.2	12.0	12.5	3.87	
4	4.12	12.5	4.03	12.2	12.5	12.5	4.03	
5	4.14	12.5	4.21	12.7	12.0	12.0	4.19	
6	4.15	12.5	4.21	12.7	12.0		4.22	
7	4.16	12.45	4.14	12.4	12.0		4.14	
8	4.17	12.4	4.24	12.7			4.26	
Mean .	4.13	12.5	4.12	12.5	12.3		4.13	

In both cases the discrepancies are within experimental error.

**127. Occurrence of the isotope effects in vibration-rotation bands of diatomic molecules.**—HCl is the only diatomic molecule whose vibration-rotation bands show the isotope effects. In the other possible cases, HBr, NO, CO, the separations are smaller than the limits of experimental refinement. Our present knowledge of isotope effects would probably not have been so precise if results from electronic bands had not been brought to bear upon the observations of vibration-rotation bands; but the intensive researches upon the (1,0) and (2,0) bands of HCl did in fact give the first proof of the phenomena and have provided the clearest illustration for those who are embarrassed by the complications of electronic bands.

**128. Applications of the isotope effect in vibration-rotation bands.**—As soon as the isotope effect was established, it became available as a method which has found various applications in the study of electronic bands.<sup>3</sup> In vibration-rotation spectra, the opportunities are more limited, since the only molecule open to investigation is HCl. Even in this limited field, however, the isotope effect has had two considerable achievements.

(i) *Confirmation of the existence of deuterium.*—When Urey, Brick-

<sup>1</sup> Hettner and Böhme, *Zeits. Physik.*, **72**, 95, 1931.

<sup>2</sup> Meyer and Levin, *Phys. Rev.*, **34**, 44, 1929.

V. p. 231.

wedde and Murphy<sup>1</sup> reported the existence of D,<sup>2</sup> it was immediately possible to confirm or deny their conclusions by work on molecular isotopes. For if D existed in the quantities suggested, there would be an appreciable number of DCl molecules in any volume of HCl, and it was clear that without using tremendous path-lengths of gas it should be possible to find the vibration-rotation bands of DCl.  $\rho$  for DCl and <sup>1</sup>HCl is very large, and so the vibrational separation must be great (the position of the centre of the (1,0) band is  $3.46\mu$  for <sup>1</sup>HCl and so can be calculated as about  $4.8\mu$  for <sup>2</sup>DCl); all difficulties of resolving the isotope components are removed.

Hardy, Barker and Dennison,<sup>3</sup> using a cell 7 metres long, found absorption in the calculated region. The structure of the band and the agreement with theoretical prediction left no doubt that the band

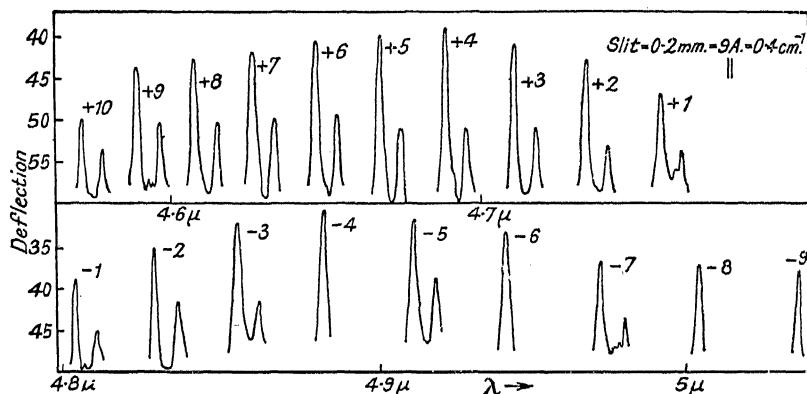


FIG. 44.—(1,0) band of DCl.  $D^{35}Cl$  and  $D^{37}Cl$  lines are clearly visible (Hardy, Barker and Dennison).

was the (1,0) vibration-rotation band of  $D^{35}Cl$ . Most of the lines in the band were accompanied by weak satellites due to  $D^{37}Cl$  (Fig. 44).

Using the measurements of Meyer and Levin upon <sup>1</sup>HCl, and an application of Fues's theory similar to that already described, Hardy, Barker and Dennison were able to construct an equation for their lines of DCl. They made the assumption that the dimensions and force fields of the molecules of <sup>1</sup>HCl and <sup>2</sup>DCl are identical; since the only difference in the force fields in the molecules is that caused by a change in nuclear spin, this assumption must be true down to the limits of hyper-fine structure. This equation was then compared with the observed frequencies and  $\rho$  adjusted to give the best fit.

Thus from Fues's theory and Meyer and Levin's measurements

<sup>1</sup> Urey, Brickwedde and Murphy, *Phys. Rev.*, **40**, 1, 1932. <sup>2</sup> V. p. 119.

<sup>3</sup> Hardy, Barker and Dennison, *ibid.*, **42**, 279, 1932.

the equations for the lines of DCl in the (1,0) band may be written

$$\nu = (2989 \cdot 24\rho^{\frac{1}{2}} - 103 \cdot 40\rho - 0 \cdot 076\rho^{\frac{3}{2}}) + (21 \cdot 1678\rho - 0 \cdot 6060\rho^{\frac{3}{2}} - 0 \cdot 005\rho^2)J - 0 \cdot 3030\rho^{\frac{3}{2}}J^2 - 0 \cdot 3020\rho^2J^3.$$

In order that this equation shall fit the observed lines, the value of  $\rho$  has to be 0.514430, which gives a final equation

$$\nu = 2090 \cdot 78 + 10 \cdot 666J - 0 \cdot 118J^2 - 0 \cdot 00056J^3.$$

The agreement between the values for the lines computed from this equation and those actually observed is very close, and the degree of error fixes the limit of accuracy of  $\rho$ , which is  $0 \cdot 514430 \pm 0 \cdot 000004$ .

From  $\rho$  the mass of  ${}^2D$  can be calculated. The final value arrived at, after certain assumption and corrections for which Hardy, Barker and Dennison's original paper should be read, is

$${}^2D = 2 \cdot 01367 \pm 0 \cdot 00010 \text{ (relative to } {}^1H = 1 \cdot 00778).$$

Correcting for the new value of  ${}^1H$ ,  ${}^2D = 2 \cdot 01437$  in fair agreement with mass spectrum results.<sup>1</sup>

(ii) *Disproof of existence of  ${}^{39}Cl$ .*—An isotope of chlorine,  ${}^{39}Cl$ , was considered possible at one time, but its existence was doubtful. It was thus of particular interest when, from a study of Meyer and Levin's curves for HCl, and from his own experimental work, Becker<sup>2</sup> concluded that the spectrum showed the presence of  $H{}^{39}Cl$ ; and this was apparently confirmed later on by Hettner and Böhme,<sup>3</sup> working on the (2,0) band.

On the other hand, the spectroscopic evidence was still not satisfactory, and Hardy and Sutherland,<sup>4</sup> using an apparatus of greater sensitivity than any other employed on the problem, made a very careful re-examination of the 2,0 band. Their results are unequivocal. The previous spectroscopic data must be regarded as untrustworthy; in conditions far more favourable for the detection of the effect due to  ${}^{39}Cl$ , Hardy and Sutherland found no trace of it. If  ${}^{39}Cl$  were present in a ratio relative to  ${}^{35}Cl$  of 1 to 1600, they would have found it. As it is, there is not the slightest spectroscopic evidence for the existence of  ${}^{39}Cl$ : and definite spectroscopic evidence that its abundance cannot be greater than this ratio [ ${}^{39}Cl : {}^{35}Cl$ , 1 : 1600].

These two investigations upon the isotope effect in vibration-rotation spectra illustrate the applications which have been made more frequently of electronic band spectra:

- (i) problems of existence of isotopes (with positive results for D, negative for  ${}^{39}Cl$ );
- (ii) problems of actual mass of isotopes (D).

<sup>1</sup> V. p. 120.

<sup>2</sup> Becker, *Zeits. Phys.*, **59**, 583 and 601, 1930.

<sup>3</sup> loc. cit.

<sup>4</sup> *Ibid.*

**129. Isotope effect in vibration-rotation spectra of polyatomic molecules.**—Isotope effects have been observed in the vibration-rotation spectra of certain polyatomic molecules containing hydrogen, e.g. H<sub>2</sub>O and D<sub>2</sub>O,<sup>1</sup> H<sub>2</sub>CO and D<sub>2</sub>CO.<sup>2</sup> In these single polyatomic molecules, the general theoretical solution for vibration-rotation is known, but the complexity of the band systems is such that assigning a particular band to a particular mode of molecular motion is still sometimes open to doubt. In such cases the bands of a heavy hydrogen isotope can serve as a valuable parallel and discriminant; as an example, the correct assignment of the bands of the H<sub>2</sub>O molecule was made much more certain when the D<sub>2</sub>O bands could be used as a comparison.<sup>3</sup>

**130. Isotope effect in electronic band spectra of diatomic molecules.**<sup>4</sup>—The total energy of a molecule can be written

$$E_e + E_v + E_r$$

where E<sub>v</sub>, E<sub>r</sub> represent the vibrational and rotational energies in the way already described, and E<sub>e</sub> is the electronic energy, which of course is of a greater order of magnitude than E<sub>v</sub> or E<sub>r</sub>. (E<sub>e</sub> > E<sub>v</sub> > E<sub>r</sub>.) Transitions between two energy states, both involving E<sub>e</sub>, E<sub>v</sub>, E<sub>r</sub>, for which

$$\hbar\nu = (E'_e + E'_v + E'_r) - (E''_e + E''_v + E''_r),$$

are those which give rise to the *electronic band spectra* of molecules, in which a single change in E<sub>e</sub>(E'<sub>e</sub> — E''<sub>e</sub>) is accompanied by a variety of changes in E<sub>v</sub> (according to the many possible values of v' — v'') each of which vibrational transitions in turn is accompanied by a variety of rotational changes J' — J''. Just as there are three sources of the transitions which give the whole band structure, there will be three different possible manifestations of the isotope effect.

(i) *The electronic isotope effect.*

The electronic transition E'<sub>e</sub> — E''<sub>e</sub> will be slightly different for different masses of one or both of the nuclei. The theory of this effect has not been worked out for even the simplest of diatomic molecules. It is, however, obvious that the effect must be very small; in practice, it has proved to be outside the range of experi-

<sup>1</sup> Barker and Sleator, *J. Chem. Phys.*, 3, 660, 1935.

<sup>2</sup> Ebers and Nielsen, *ibid.*, 6, 311, 1938.

<sup>3</sup> Darling and Dennison, *Phys. Rev.*, 57, 128, 1940.

<sup>4</sup> In this part of the chapter particularly, and also in many other ways, the writer is greatly indebted to Dr. Jevons's *Report on Band Spectra of Diatomic Molecules*. The isotope section of this book, to which reference should be made, is up to the very high level of clarity and comprehensiveness which distinguishes the whole work. The general position of the isotope effect in diatomic molecules has not been substantially altered since the Report appeared.

mental observation. Presumably, in the band spectra of isotopic molecules each line has a sort of isotopic hyperfine structure of separations less than  $\cdot01 \text{ cm}^{-1}$ . For all present purposes, this can be completely ignored.

(ii) *The vibrational isotope effect.*

(iii) *The rotational isotope effect.*

These will apply in precisely the manner developed for vibration-rotation spectra. And so, since the electronic effect is negligible, the total isotope effect in electronic band spectra will be the algebraic sum of the vibration and rotation isotopic effects, exactly as in the vibration-rotation bands of HCl.

The vibrational isotopic effect, which is much larger,<sup>1</sup> has been much the more important in the history of band spectra. The form it takes in electronic bands follows at once from the equation (3),<sup>2</sup> from which it is clear that the vibrational isotope effect is constant

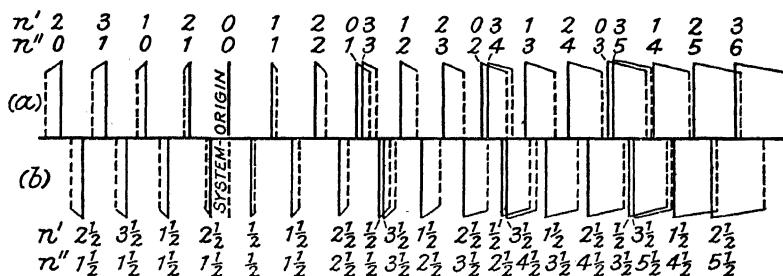


FIG. 45.—Typical Pattern of Vibrational Isotope Effect in Electronic Bands. (After Mulliken.)

for the lines of a given band (given values of  $v'$ ,  $v''$  and  $v$ ), and that the isotopic displacement increases linearly from band to band with the interval  $v_v$ .

A diagram reproduced from one of Mulliken's early papers shows these results (Fig. 45). The case illustrated is that when the heavier molecule is the more abundant, as in  $^{11}\text{B}^{16}\text{O}$ ,  $^{10}\text{B}^{16}\text{O}$  and  $\rho - 1$  is negative: the band sequences are overlapping. The comparison between (a) and (b) was designed to show the difference between the effect for whole and half quantum numbers.

The magnitude of the vibrational isotopic displacement varies with the atomic weights, with  $\rho - 1$ , which itself is approximately proportional to  $M - M^i$  (when  $M$ ,  $M^i$  are the masses of the atomic isotopes in the molecules).

Another of Mulliken's diagrams illustrates this effect of mass (Fig. 46).

<sup>1</sup> V. p. 223.

<sup>2</sup> V. p. 222.

The rotational isotope effect was shown to depend on  $\rho^2 - 1$ . The variation of the effect with  $J$ , the rotational quantum number,

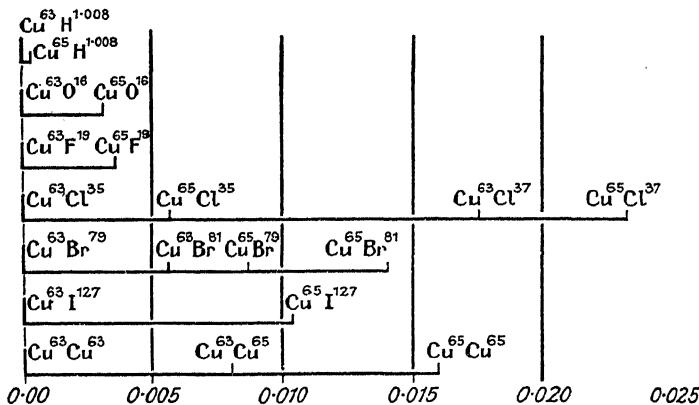


FIG. 46.—Calculated Values of  $\rho - 1$  for Copper Compounds. (From Mulliken.)

is demonstrated in Fig. 47. The full curves represent the hypothetical bands for the more abundant of two isotopic molecules; for each

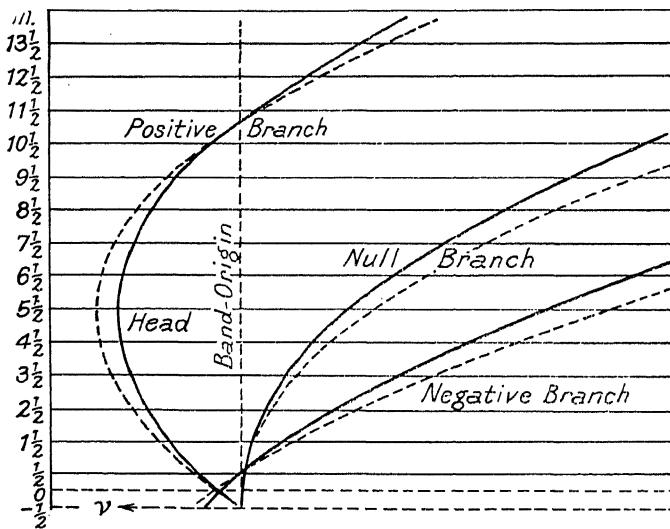


FIG. 47.—Rotational Isotope Effect in Electronic Bands, shown as a Forstrat Diagram.

value of  $J$ , the less abundant molecule has a different rotational shift illustrated by the dotted curves.

Since  $\nu_r$  is so much smaller than  $\nu_e$ , the rotational isotope effect

is smaller than the vibrational : and it is usual to determine  $\rho$  from a study of the vibrational effect alone, by measuring the displacements of lines of small  $J$ , for which the rotational shift is negligible.

**131. Applications of the isotope effect in electronic bands of diatomic molecules.**—As in the example of  $^2D$  already discussed under vibration-rotation spectra, there is one application of the isotope effect which is of great general interest. Several rare isotopes have been discovered from the isotope effect in band spectra. In fact the unequivocal identification of a number of isotopes has been the chief spectroscopic contribution to the subject.

(i) *Discovery of new isotopes.*

The procedure described for DCl is also quite representative of the search for isotopes in electronic band spectra. Sometimes, of course, the discovery of an isotopic spectrum has been a matter of chance ; instead of going out to look in a calculated position for a spectrum of given structure, workers have found satellite bands which later were proved to be isotopic components. However, after the initial recognition of the bands, the method of Hardy, Barker and Dennison is substantially that used for the discovery of isotopes since Mulliken<sup>1</sup> proved the existence of  $^{30}Si$ . In all cases, the construction of an equation derived from the principal band and involving  $\rho$ , the proof or disproof that this equation can account for the observed lines, and the evaluation of  $\rho$ , are standard operations.

Some of the most interesting of recent results are those on the isotopes of oxygen, nitrogen, carbon and beryllium. For fuller details, reference should again be made to Jevons's monograph, but a brief description is desirable here.

*Oxygen.*—Close to the well-known red atmospheric bands of  $O_2$  ( $^3\Sigma \rightarrow ^1\Sigma$ ) Dieke and Babcock<sup>2</sup> observed a weaker band of very much the same structure. Giauque and Johnston<sup>3</sup> showed that these lines could be interpreted as due to  $^{18}O^{16}O$ , the calculated isotopic shifts agreeing extremely well with the observed separations. There are also twice as many rotational lines in the  $^{18}O^{16}O$  band as in the  $^{16}O^{16}O$  band, as required by the theory of symmetrical and anti-symmetrical terms.

Babcock<sup>4</sup> showed also that another system of weak lines near to the main band could be explained as due to  $^{17}O^{16}O$ .

<sup>1</sup> Mulliken, *Phys. Rev.*, **26**, 319, 1925.

<sup>2</sup> Dieke and Babcock, *P.N.A.S.*, **13**, 670, 1927.

<sup>3</sup> Giauque and Johnston, *Nature*, **123**, 318 and 831, 1929.

<sup>4</sup> Babcock, *ibid.*, **123**, 761, 1929.

TABLE XVIII

## A SUMMARY OF OBSERVATIONS OF THE ISOTOPE EFFECT IN DIATOMIC SPECTRA

Element.	Atomic Number.	Atomic Weight.	Mass Numbers. M M'	Abundance Ratio. a : 1	Band-Systems.	Isotopic Molecules. MM' M'M'	$\rho - 1$ .
H	1	1.008	1 2		HCl infra-red	$^1\text{H}^{35}\text{Cl}$ $^1\text{H}^{37}\text{Cl}$	-0.51443
Li	3	6.940	7 6	12.3 : 1	LiH Li <sub>2</sub> , blue-green	$^7\text{LiH}$ $^7\text{Li}^7\text{Li}$	+0.01036 +0.04083
B	5	10.82	11 10	4 : 1	BH, $\lambda$ 4100 BO $\alpha$ and $\beta$	$^{11}\text{BH}$ $^{11}\text{B}^{16}\text{O}$	+0.01942 +0.02098
C	6	12.010	12 13	90 : 1	C <sub>2</sub> , Swan CN, Violet CO, fourth positive	$^{12}\text{C}^{12}\text{C}$ $^{12}\text{C}^{14}\text{N}$ $^{12}\text{C}^{16}\text{O}$ $^{13}\text{C}^{13}\text{C}$	-0.01942 -0.02093 -0.0223
N	7	14.008	14 15	285 : 1	N <sub>2</sub> , second positive NO, $\gamma$	$^{14}\text{N}^{14}\text{N}$ $^{14}\text{N}^{16}\text{O}$	-0.01881 -0.01794
O	8	16.000	16 18 17	500 : 1	NO, $\gamma$ O <sub>2</sub> , atmospheric	$^{16}\text{O}^{14}\text{N}$ $^{16}\text{O}^{16}\text{O}$	-0.02627 -0.01382 -0.02818 -0.01482
Mg	12	24.32	24 25 26	7 : 1	MgH, $\lambda$ 5211 MgH <sup>+</sup>	$^{24}\text{MgH}$ $^{24}\text{MgH}^+$	-0.00080 -0.00154 -0.00080 -0.00154
Si	14	28.06	28 29 30		SiN	$^{28}\text{Si}^{14}\text{N}$ $^{29}\text{Si}^{14}\text{N}$	-0.00578 -0.01117
Cl	17	35.457	35 37	3.07 : 1	HCl infra-red Cl <sub>2</sub> visible absorption CaCl CuCl, four systems SrCl AgCl ultraviolet SnCl two ultraviolet systems ICl red absorption BaCl AuCl two systems HgCl TiCl absorption	$^{35}\text{ClH}$ $^{35}\text{Cl}^{35}\text{Cl}$ $^{35}\text{Cl}^{40}\text{Ca}$ $^{35}\text{Cl}^{63}\text{Cu}$ $^{35}\text{Cl}^{65}\text{Cu}$ $^{35}\text{Cl}^{88}\text{Sr}$ $^{35}\text{Cl}^{88}\text{Sr}$ $^{35}\text{Cl}^{107}\text{Ag}$ $^{35}\text{Cl}^{109}\text{Ag}$ $^{35}\text{Cl}^{119}\text{Sn}$ $^{35}\text{Cl}^{127}\text{I}$ $^{35}\text{Cl}^{139}\text{Ba}$ $^{35}\text{Cl}^{139}\text{Ba}$ $^{35}\text{Cl}^{197}\text{Au}$ $^{35}\text{ClHg}$ $^{35}\text{ClTI}$	-0.00075 -0.01361 -0.01452 -0.010753 -0.01772 -0.01940 -0.01953 -0.02058 -0.02067 -0.02111 -0.02142 -0.02173 -0.02180 -0.02322 -0.02328 -0.02334
K	19	39.096	39 41	14 : 1	K <sub>2</sub> Orange-red	$^{39}\text{K}^{39}\text{K}$ $^{41}\text{K}^{39}\text{K}$	-0.01223

TABLE XVIII—(continued)

Element.	Atomic Number.	Atomic Weight.	Mass Numbers. M M'	Abundance Ratio. a : 1	Band-Systems.	Isotopic Molecules. MM' M'M'	$\rho - 1$ .
Cu	29	63.57	63 65	2.5 : 1	CuH, $\lambda\lambda$ 4280, 4328 CuF CuCl, four sys- tems CuBr, three sys- tems CuI	$^{63}\text{CuH}$ $^{65}\text{CuH}$ $^{63}\text{Cu}^{19}\text{F}$ $^{65}\text{Cu}^{19}\text{F}$ $^{63}\text{Cu}^{35}\text{Cl}$ $^{65}\text{Cu}^{35}\text{Cl}$ $^{63}\text{Cu}^{37}\text{Cl}$ $^{65}\text{Cu}^{37}\text{Cl}$ $^{63}\text{Cu}^{79}\text{Br}$ $^{65}\text{Cu}^{79}\text{Br}$ $^{63}\text{Cu}^{81}\text{Br}$ $^{65}\text{Cu}^{81}\text{Br}$ $^{63}\text{Cu}^{127}\text{I}$ $^{65}\text{Cu}^{127}\text{I}$	-0.00024 -0.00357 -0.00551 -0.00571 -0.00860 -0.00869 -0.01034
Zn	30	65.38	64 66		ZnI	$^{64}\text{Zn}^{127}\text{I}$ $^{66}\text{Zn}^{127}\text{I}$	-0.1032
Ge	32	72.60	74 72 76		GeS absorption	$^{74}\text{Ge}^{32}\text{S}$ $^{76}\text{Ge}^{32}\text{S}$ $^{72}\text{Ge}^{32}\text{S}$ $^{76}\text{Ge}^{32}\text{S}$	+0.00859 +0.00419 -0.00398
Br	35	79.916	79 81	1 : 1	CuBr, three sys- tems Br, visible ab- sorption SrBr AgBr BaBr HgBr TlBr absorption	$^{79}\text{Br}^{63}\text{Cu}$ $^{81}\text{Br}^{43}\text{Cu}$ $^{79}\text{Br}^{65}\text{Cu}$ $^{81}\text{Br}^{65}\text{Cu}$ $^{79}\text{Br}^{81}\text{Br}$ $^{79}\text{Br}^{89}\text{Br}$ $^{81}\text{Br}^{81}\text{Br}$ $^{79}\text{Br}^{86}\text{Sr}$ $^{81}\text{Br}^{86}\text{Sr}$ $^{79}\text{Br}^{88}\text{Sr}$ $^{81}\text{Br}^{88}\text{Sr}$ $^{79}\text{Br}^{107}\text{Ag}$ $^{81}\text{Br}^{107}\text{Ag}$ $^{79}\text{Br}^{109}\text{Ag}$ $^{81}\text{Br}^{109}\text{Ag}$ $^{79}\text{Br}^{135}\text{Ba}$ $^{81}\text{Br}^{135}\text{Ba}$ $^{79}\text{Br}^{138}\text{Ba}$ $^{81}\text{Br}^{138}\text{Ba}$ $^{79}\text{Br}^{202}\text{Hg}$ $^{81}\text{Br}^{202}\text{Hg}$ $^{81}\text{BrTl}$ $^{79}\text{BrTl}$	-0.00549 -0.00559 +0.00623 -0.00627 -0.00646 -0.00653 -0.00713 -0.00724 -0.00784 -0.00788 -0.00897 +0.00900
Sr	38	87.63	88 86	8.4 : 1	SrF yellow-green SrCl SrBr	$^{88}\text{Sr}^{19}\text{F}$ $^{86}\text{Sr}^{19}\text{F}$ $^{88}\text{Sr}^{35}\text{Cl}$ $^{86}\text{Sr}^{35}\text{Cl}$ $^{88}\text{Sr}^{37}\text{Cl}$ $^{86}\text{Sr}^{37}\text{Cl}$ $^{88}\text{Sr}^{79}\text{Br}$ $^{86}\text{Sr}^{79}\text{Br}$ $^{88}\text{Sr}^{81}\text{Br}$ $^{86}\text{Sr}^{81}\text{Br}$	+0.00206 +0.00330 +0.00344 +0.00549 +0.00556
Ag	47	107.880	107 109	1 : 1	AgH AgCl AgBr AgI	$^{107}\text{AgH}$ $^{109}\text{AgH}$ $^{107}\text{Ag}^{35}\text{Cl}$ $^{109}\text{Ag}^{35}\text{Cl}$ $^{107}\text{Ag}^{37}\text{Cl}$ $^{109}\text{Ag}^{37}\text{Cl}$ $^{107}\text{Ag}^{79}\text{Br}$ $^{109}\text{Ag}^{79}\text{Br}$ $^{107}\text{Ag}^{81}\text{Br}$ $^{109}\text{Ag}^{81}\text{Br}$ $^{107}\text{Ag}^{127}\text{I}$ $^{109}\text{Ag}^{127}\text{I}$	-0.00001 -0.00226 -0.00236 -0.00390 -0.00398 -0.00499
Ba	56	137.36	138 136		BaCl BaBr	$^{138}\text{Ba}^{35}\text{Cl}$ $^{136}\text{Ba}^{35}\text{Cl}$ $^{138}\text{Ba}^{37}\text{Cl}$ $^{136}\text{Ba}^{37}\text{Cl}$ $^{138}\text{Ba}^{79}\text{Br}$ $^{136}\text{Ba}^{79}\text{Br}$ $^{138}\text{Ba}^{81}\text{Br}$ $^{136}\text{Ba}^{81}\text{Br}$	+0.00149 +0.00155 +0.00267 +0.00272
Hg	80	200.61	202 200 204		HgII, $^2\text{H}_2 \longrightarrow 2\Sigma$	$^{198}\text{HgH}$ $^{200}\text{HgH}$ $^{202}\text{HgH}$ $^{204}\text{HgH}$	+0.000050 +0.000025 -0.000024
Pb	82	207.21	208 206 207	7 : 4 7 : 3	PbO Systems A and C	$^{203}\text{Pb}^{16}\text{O}$ $^{204}\text{Pb}^{16}\text{O}$ $^{207}\text{Pb}^{16}\text{O}$	+0.00035 +0.00017

From the values of  $\rho$ , obtained in a similar way to that described for DCl, the mass of  $^{18}\text{O}$  is calculated to be 18.0065 on the basis of  $^{16}\text{O} = 16$ ; the mass of  $^{17}\text{O}$  is 17.0029.

After these results upon the  $\text{O}_2$  bands had been reported, Naudé<sup>1</sup> made a search of the  $^2\Sigma \leftarrow ^2\Pi$  system of NO, and found bands due to  $^{14}\text{N}^{17}\text{O}$  and  $^{14}\text{N}^{18}\text{O}$ .

*Nitrogen.*—As well as finding the bands of oxygen isotopes in NO, Naudé also discovered the bands of  $^{15}\text{N}^{16}\text{O}$  in the same system. This was confirmed by Herzberg<sup>2</sup> from a study of the  $^3\Pi \rightarrow ^3\Pi$  bands of  $\text{N}_2$ .

*Carbon.*—In a study of the Swan bands, King and Birge<sup>3</sup> discovered bands which they proved due to  $^{13}\text{C}^{12}\text{C}$ . [Plate XII gives a very beautiful illustration of part of the main  $^{12}\text{C}^{12}\text{C}$  band and the isotopic component.] The value of  $\rho$  gives a mass of  $^{13}\text{C} = 13$  very nearly (on the basis of  $^{12}\text{C} = 12$ ).

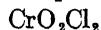
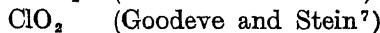
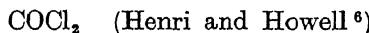
The isotope  $^{13}\text{C}$  was also proved present in the fourth positive bands of CO and the violet bands of CN.

*Beryllium.*—Watson<sup>4</sup> has suggested that lines due to  $^8\text{BeH}$  occur in the  $^2\Pi \rightarrow ^2\Sigma$  system of BeH. The case put forward, though ingenious and suggestive, has to introduce more assumptions than are necessary in the other examples: and further experimental work by Olsson<sup>5</sup> indicates that  $^8\text{BeH}$  lines are not present. The spectroscopic evidence for  $^8\text{Be}$  cannot be taken as definite.

#### (ii) Other applications of the isotope effect.

The isotope effect has some important applications in technical spectroscopy, for instance in identifying the molecule responsible for a band system and in assigning ( $v'$ ,  $v''$ ) values to bands in a system. Jevons's monograph includes a clear exposition of these methods.

**132. The isotopic effect in the electronic band spectra of polyatomic molecules.**—Henri first showed an indubitable isotope effect in the band spectrum of  $\text{COCl}_2$ . Since then, the phenomenon has been observed in the bands of several molecules containing chlorine, e.g.



<sup>1</sup> Naudé, *Phys. Rev.*, **36**, 333, 1930.

<sup>2</sup> Herzberg, *Zeits. Phys. Chem.*, **9B**, 43, 1930.

<sup>3</sup> King and Birge, *Nature*, **124**, 127, 1929, and *Astrophys. J.*, **72**, 19, 1930.

<sup>4</sup> Watson and Parker, *Phys. Rev.*, **36**, 1019, 1930.

<sup>5</sup> Olsson, *Zeits. Phys.*, **73**, 732, 1932.

<sup>6</sup> Henri and Howell, *Proc. Roy. Soc., A*, **128**, 178, 1930.

<sup>7</sup> Goodeve and Stein, *Trans. Farad. Soc.*, **73**, 1929.

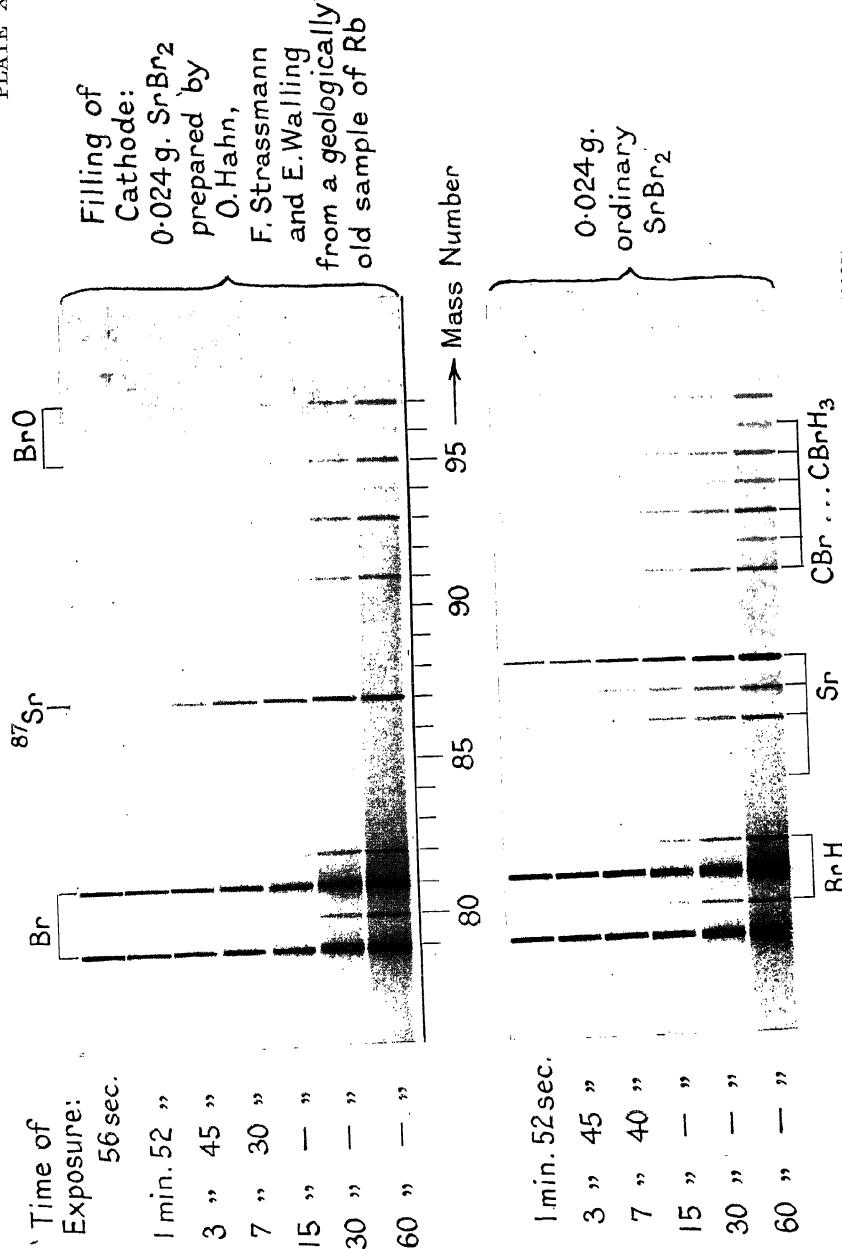


PLATE XII

$\lambda 4737$

$\lambda 4744.5$

$C^{13}C^{12}$

$C^{12}C^{12}$



ISOTOPE EFFECT IN OPTICAL SPECTRA

Upper : Band Spectra of Carbon.  
Lower :  $H\alpha$ - and  $H\beta$ -Lines of Hydrogen.

Fig. 48, showing part of a band in  $\text{CrO}_2\text{Cl}_2$ , illustrates the appearance of the effect. The theory is rather complicated: for each of the possible nuclear vibrations the isotope effect may be different, and will only be the same for reasons of symmetry: obviously in a molecule like  $\text{ClX}_2$ , in which the nuclei are considered to be in a straight line, the symmetrical vibration of the X's along the axis  $\text{X} \rightarrow \text{Cl} \leftarrow \text{X}$

↑  
will give no isotope effect at all, and the vibrations  $\text{X} - \text{Cl} - \text{X}$

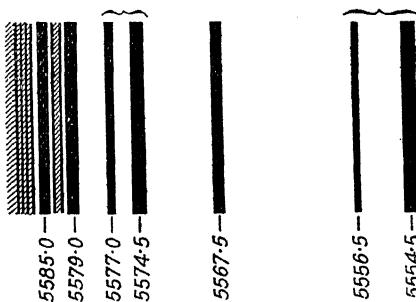


FIG. 48.—Isotope Effect in a Polyatomic Molecule.

Sketch of a typical arrangement of lines in the electronic bands of  $\text{CrO}_2\text{Cl}_2$  (as studied by C.P.S.). Note the isotope pairs (5577, 5574.5) and (5556.5, 5554.5).

and  $\text{X} \rightarrow \text{Cl} \rightarrow \text{X}$  will give different isotope effects. For these and other reasons, little progress has yet been made in the analysis of isotope effects in the electronic spectra of polyatomic molecules.

In Table XVIII are summarized some of the principal results so far obtained from the investigation of the isotope effect in band spectra.

## CHAPTER XV

### THE ISOTOPE EFFECT IN ATOMIC SPECTRA

Isotope effects do not play an important part in atomic spectra. There are, however, two ways, one direct and one indirect, in which the presence of isotopes may show themselves.

**133. The electronic isotope effect.**—For atoms or ions which consist of a single electron revolving round a nucleus of mass  $M$ , the principal spectral lines will be given by Bohr's equation

$$\nu = \frac{2\pi^2 E^4}{ch^3} \frac{Mm_e}{M + m_e} \left( \frac{1}{n''^2} - \frac{1}{n'^2} \right) \quad \dots \quad (1)$$

where  $n'$  and  $n''$  are the principal quantum numbers of the upper and lower states, and  $E = e, 2e, 3e, 4e \dots$  for  $H, He^+, Li^{++}$

Obviously, if the nucleus exists in the isotopic masses  $M$  and here will be satellite lines represented by :

$$\nu' - \nu = \frac{2\pi^2 E^4}{ch^3} \left( \frac{M^i m_e}{M^i + m_e} - \frac{M m_e}{M + m_e} \right) \left( \frac{1}{n''^2} - \frac{1}{n'^2} \right) \div \frac{m_e(M^i - M)\nu}{MM^i} \quad \dots \quad (2)$$

This relation was put to a dramatic use in the discovery of deuterium. Urey, Brickwedde and Murphy <sup>1</sup> calculated that, if this isotope existed, there would be isotopic components of the Balmer lines shifted to the short wave-length side of  ${}^1H\alpha, \beta, \gamma, \delta$  by 4.16, 5.61, 6.29 and 6.65 cm<sup>-1</sup> respectively. The successful result of their search for these lines is beautifully illustrated by Plate XII. In this plate  ${}^1H\alpha$  and  ${}^2D\alpha, {}^1H\beta$  and  ${}^2D\beta$  all appear and are separated by exactly the calculated distance.

In itself, the appearance of a very weak line near each Balmer line would not have been quite convincing; but Urey and his colleagues made their proof definite by preparing three samples of hydrogen in which the proportions of D—if any existed—had been raised by fractional distillations and by showing that the intensities of the lines in the positions calculated for D were in agreement with

<sup>1</sup> *Phys. Rev.*, **40**, 1, 1932.

the proportion of D believed to be in the samples. Thus, on the assumption that D existed, their third sample was prepared so as to be considerably richer in D than the others; and this sample gave much enhanced lines at the wave-lengths calculated for D. After these experiments, there was no doubt that D existed.

The D line has the doublet structure which, of course, was anticipated. The comparison of the positions of the lines calculated from equation (2) and actually observed, is shown in Table XIX.

TABLE XIX

	H <sub>α</sub> .	H <sub>β</sub> .	H <sub>γ</sub> .	H <sub>δ</sub> .
Calculated displacement . . .	1.743	1.326	1.185	1.119 cm <sup>-1</sup>
Observed :				
Ordinary Hydrogen . . .	—	1.346	1.206	1.145
Sample I . . .	—	1.230	1.191	1.103
Samples II and III : : :	1.791	1.313	1.176	1.088

A rough estimate of the proportions of D in ordinary hydrogen gave a value of 1 in 4000 or less, but the figure was only a crude approximation.

Equation (2) can only be used with accuracy in the case of hydrogen; and it ceases to apply at all when the atom has more than one electron outside the nucleus. For two-electron and three-electron atoms the theory has been worked out by Hughes and Eckart.<sup>1</sup> The separations of <sup>7</sup>Li - <sup>6</sup>Li have been measured by Hughes<sup>2</sup> and shown to be in reasonable agreement with the theoretical predictions. Hughes's observations were :

$$\text{Li}^+ : 2^3\text{P} \rightarrow 1^3\text{S} : \nu^i - \nu = -1.06 \text{ cm}^{-1} \text{ (to longer } \lambda)$$

$$\text{Li} : 2^3\text{P} \rightarrow 1^3\text{S} : \nu^i - \nu = -0.345 \text{ cm}^{-1}$$

$$\text{Li} : 3^3\text{P} \rightarrow 1^3\text{S} : \nu^i - \nu = -0.56 \text{ cm}^{-1}.$$

The theory of the effect for an atom with more than three electrons has not been established; and there are few observations, perhaps only those upon the lines of neon, which demonstrate the effect experimentally for such atoms. The effect will obviously be very small, and it is always likely to be confused with the hyper-fine structures.

**134. The effect of the nuclear spin of isotopes.**—The spectroscopic effects discussed up to now (the vibrational and rotational effects in band spectra and the electronic effect in line spectra) have been caused entirely by the differences in mass of the isotopic nuclei.

<sup>1</sup> Hughes and Eckart, *Phys. Rev.*, 36, 694, 1930.

<sup>2</sup> Hughes, *ibid.*, 38, 857, 1931.

There is one other difference in isotopic nuclei which may be revealed spectroscopically : the spin moments of isotopic nuclei may not be the same, and accordingly the features of the spectra which depend on nuclear spin may show differences for different isotopes.

The values of the nuclear spin of different isotopes have now been measured for several elements : and these facts have been important in developing the present tentative theory of nuclear structure. It is appropriate here to describe in outline the methods by which the nuclear spins have been found.

**135. Hyper-fine structures of atomic line spectra.**—Many spectral lines, particularly those of heavy atoms, show a narrow structure with separations less than  $1 \text{ cm}^{-1}$ . This "hyper-fine structure" may be, and probably is, due to more than one cause ; but it cannot be explained in terms of electronic states alone ; whatever the cause is, it is necessary to invoke some interaction of the electrons with the *nucleus*.

It is possible that the presence of isotopic nuclei produces some of these hyper-fine structures, perhaps in the way mentioned on p. 236. On the other hand, the presence of isotopes cannot be all the truth, for hyper-fine structure is clearly marked for atoms which have no isotopes. Thus, as an explanation for the greater number, though not all, of hyper-fine structures, the idea of nuclear spin has been adopted. Pauli first pointed out that if a mechanical moment of the nucleus were assumed, there would, of course, be an associated magnetic moment, whose interaction with the extra-nuclear electrons could be used to explain the hyper-fine splitting. The magnetic moment will probably be of the order of  $m/M$  that of the electron, which would give an observable hyper-fine separation for heavy atoms. The mechanical moment can be represented by  $i\hbar/2\pi$  where  $i$  is the nuclear spin quantum number.

The interaction of the nuclear and electronic moments, and the production of hyper-fine levels, can be illustrated in the usual imperfect but useful way by a vector model.

With  $i$  the mechanical moment of the nucleus and  $j$  the mechanical moment of the electron, the resultant of  $i$  and  $j$  will assume different values, in the normal process of addition of vectors. The resultant can be called  $f$  (the hyper-fine quantum number). The number of levels will be  $2j + 1$  if  $j < i$  and  $2i + j$  if  $i < j$ .

As an example,

$$\begin{aligned} \text{if } i = \frac{5}{2} \\ \text{and } j = \frac{1}{2}, \end{aligned}$$

$f$  assumes two values, 2 and 3, in the ordinary vector summation. Very much the same considerations apply as for the vector formation

of  $j$  from  $l$  and  $s$ ; and so the selection rule will be  $\Delta f = \pm 1, 0$ , and  $f = 0 \rightarrow f = 0$  is forbidden.

The separation formulæ have been definitely established for configurations with a deeply penetrating  $s$  electron, but are otherwise liable to change with the production of new data, and it would be out of place to consider them here.

However, it is possible to describe how  $i$  is obtained from measurements of hyper-fine structure in a case where there seem to be fewer complications than in most atoms—Bi.

Goudsmit and Back<sup>1</sup> made a very satisfying examination of the hyper-fine structure of a number of lines in the spectrum of Bi: they succeeded in assigning hyper-fine levels which explained the structure observed simply and naturally.

Thus a scheme on the following lines:

$f = 3$	_____	
4	_____	
5	_____	$(6p)^3 \ ^2D_{\frac{3}{2}} j = \frac{3}{2}$
6	_____	
7	_____	
6	_____	
5	_____	$(6p)^3 \ ^2D_{\frac{5}{2}} = \frac{5}{2}$
4	_____	
3	_____	
2	_____	
5	_____	$(6p)^3 \ ^2P_{\frac{1}{2}} j = \frac{1}{2}$
4	_____	
5	_____	$2s^2 \quad j = \frac{1}{2}$
4	_____	
4	_____	$3s \quad j = \frac{1}{2}$
5	_____	
4	_____	$3d'''' \quad j = \frac{1}{2}$
5	_____	
$f = 6$	_____	$4d'' \quad j = \frac{3}{2}$
5	_____	
4	_____	
3	_____	

<sup>1</sup> Goudsmit and Back, *Zeits. Phys.*, 43, 321, 1927.

<sup>2</sup> These four levels are denoted by a non-committal notation, since they are not known unequivocally.

In each case the number of  $f$  bands is  $2j + 1$ , in accordance with the theory : and transition between these levels, with  $f = \pm 1, 0$  gives exactly the hyper-fine structure observed for  $\lambda 4722$  Bi, ( ${}^2D_{\frac{3}{2}} - {}^2S$ ), etc. The six-fold structure of  $\lambda 4722$ , predicted by the above scheme, is actually observed.

Since for the level where  $j = \frac{5}{2}$  there are  $2j + 1$  hyper-fine levels, then  $i$  must be equal to or larger than  $\frac{5}{2}$ .

In order to determine  $i$  definitely, Back measured the Zeeman effect of the hyper-fine structure. In the case where the external magnetic field is strong, the theory is simple. The interaction of  $i$  and  $j$  with the field is much greater than with one another. That is, the coupling between  $i$  and  $j$  is broken and each has its quantized projection on the external field, H. The component of  $i$  along H can be called  $m_i$ , and of  $j$ ,  $m_j$ . Then the magnetic state can be written

$$W_H = \frac{e\hbar}{4\pi m_0 c} H(m_i g(i) + m_j g)$$

where  $g$  is the Landé factor.  $g(i)$  will be very small, since the factor  $m_e/M$  enters, and  $m_i g(i)$  will be undetectable. So, to a first approximation, the Zeeman effect is the same with a nuclear moment as without. If, however, we include the interaction of the magnetic nucleus and the extra-nuclear electrons we have to write the total interaction energy as—

$$W = \frac{e\hbar}{4\pi m_0 c} H \{ m_i g(i) + m_j g \} + Aij \cos \bar{i}\bar{j}$$

where  $m_i g(i)$  is negligibly small and  $A$  is the separation constant. For a strong field, the second term is smaller than the first.

$ij \cos \bar{i}\bar{j}$  becomes  $m_i m_j$ , and the expression for the energy is

$$E = \frac{e\hbar}{4\pi m_0 c} m_j g + Am_i m_j$$

The first term is the ordinary Zeeman effect, and so with every Zeeman level there will be a hyper-fine structure determined by  $Am_i m_j$ ;  $m_i$  can assume all the  $2i + 1$  values from  $-i \dots +i$ . Thus every Zeeman level will be split into  $2i + 1$  equidistant levels with a separation of  $Am_i$ ; and since  $m_i$  does not change during a transition, each of the  $2i + 1$  levels of the initial Zeeman state combines with only one of the  $2i + 1$  levels of the upper state. Thus the Zeeman lines themselves have a very simple pattern : each Zeeman component is split into a hyper-fine structure of  $2i + 1$  equidistant lines.

Accordingly if the Zeeman effect of the hyper-fine structure can be measured, the number of hyper-fine lines in each component gives an unambiguous value of  $i$ . Back resolved the hyper-fine structure

of four Zeeman components of  $\lambda 4722$  of Bi. Each was split into ten components and so for the bismuth nucleus  $2i + 1 = 10$  and  $i = \frac{9}{2}$ .

The greater number of nuclear spins so far known have been measured in this way, though few with such definiteness. Apart from the method of hyper-fine structure there are two other quite distinct ways of determining nuclear spins.

**136. Nuclear spins from alternating intensities in molecular spectra.**—The rotational levels of a completely symmetrical molecule fall into two classes, called symmetrical ( $s$ ) and anti-symmetrical ( $a$ ), which depend upon properties of the wave function. Transition can only take place between  $s$  and  $s$  and  $a$  and  $a$  levels. Now the statistical weight of an anti-symmetrical level  $J$  is less than the mean of the weights of the neighbouring symmetrical levels of  $J + 1$  and  $J - 1$ , i.e. the levels have two sets of statistical weights

$$g_s(2J + 1) \text{ and } g_a(2J + 1) \text{ and } g_s > g_a$$

In this way the  $s$  and  $a$  levels can be thought of as *strong* and *weak* levels, and transitions between them will give *strong* and *weak* lines—the well-known alternating intensities in the spectrum of symmetrical molecules. An unsymmetrical molecule (such as NO and  $^{35}\text{Cl}^{37}\text{Cl}$ ) will have rotational levels all of statistical weight  $2J + 1$ , and the phenomenon of alternating intensities disappears.

The occurrence of  $s$  and  $a$  levels depends upon the existence of a nuclear moment, in such a way that

$$\frac{g_s}{g_a} = \frac{i+1}{i}.$$

In the particular case where the anti-symmetrical levels are not present at all, as in  $\text{O}_2$ , then obviously  $i = 0$ . In other cases, where the  $a$  levels are present but weaker than the  $s$  levels, it is possible, by evaluating the relative intensities and allowing for the ordinary  $(2J + 1)$  factor, to obtain a value for  $g_s/g_a$  and accordingly calculate  $i$ .

Investigations of some symmetrical diatomic molecules and their corresponding isotopic molecules ( $^{35}\text{Cl}^{35}\text{Cl}$ ,  $^{35}\text{Cl}^{37}\text{Cl}$ :  $^6\text{Li}^7\text{Li}$ ,  $^6\text{Li}^7\text{Li}$ :  $^{79}\text{Br}^{79}\text{Br}$ ,  $^{81}\text{Bi}^{81}\text{Br}$ ,  $^{79}\text{Bi}^{81}\text{Br}$ ) gave a striking demonstration of the correctness of Hund's theory. It was found that for the unsymmetrical molecules the intensities were no longer alternating, and for  $^{35}\text{Cl}^{37}\text{Cl}$  were as regular as for CO.

When nuclear spins calculated from band spectra can be compared to those from hyper-fine structure ( $^7\text{Li}$ ,  $^{79}\text{Br}$ ,  $^{81}\text{B}$ ), the results agree.<sup>1</sup> This is satisfactory, for in the method of hyper-fine structure

<sup>1</sup> The results for bromine, however, are rather nebulous, and there is no completely satisfactory case where the two methods have been applied to the same nucleus.

TABLE XX  
NUCLEAR SPINS

Atomic Number.	Element.	Mass Number.	Nuclear Spin.	Method.
1	H	1	$\frac{1}{2}$	Alt. int.
	D	2	1	
2	He	4	0	Alt. int.
3	Li	6	$\frac{1}{2}$	Hyp. str. Atomic beams. Alt. int. Hyp. str.
	Li	7	$\frac{1}{2}$	
5	B	10	$\frac{1}{2}$	Inferred from molecular beams.
		11	$\frac{1}{2}$	
6	C	12	0	Alt. int.
	C	13	$\frac{1}{2}$	
7	N	14	$\frac{1}{2}$	Alt. int.
	N	15	$\frac{1}{2}$	
8	O	16	0	Alt. int.
9	F	19	$\frac{1}{2}$	Alt. int.
11	Na	23	$\frac{1}{2}$ or $\frac{3}{2}$	Alt. int. and atomic beams (disagreement: $\frac{3}{2}$ probable) Inferred from molecular beams.
13	Al	27	$\frac{1}{2}$	Alt. int.
15	P	31	$\frac{1}{2}$	Alt. int.
16	S	32	0	Alt. int.
17	Cl	35	$\frac{1}{2}$	Alt. int.
19	K	39	$> \frac{1}{2}$	Alt. int.
25	Mn	55	$\frac{5}{2}$	Hyp. str.
29	Cu	63	$\frac{3}{2}$	Hyp. str.
	Cu	65	$\frac{5}{2}$	
31	Ga	69	$\frac{3}{2}$	Hyp. str.
	Ga	71	$\frac{5}{2}$	
33	As	75	$\frac{3}{2}$	Hyp. str.
35	Br	79	$\frac{3}{2}$	Hyp. str. and alt. int.
	Br	81	$\frac{5}{2}$	
37	Rb	85	$\frac{5}{2}$	Hyp. str.
	Rb	87	$\frac{7}{2}$	
48	Cd	111, 113	$\frac{1}{2}$	Hyp. str.
	Cd	110, 112, 114, 116	0	
49	In	115	$\frac{3}{2}$	Hyp. str. Atomic beams.
51	Sb	121	$\frac{1}{2}$	Hyp. str.
		123	$\frac{3}{2}$	
53	I	127	$\frac{3}{2}$	Hyp. str. (and alt. int.)
55	Cs	133	$\frac{7}{2}$	Hyp. str.
56	Ba	137	$\frac{3}{2}$	Hyp. str.
	Ba	136, 138	0	
57	La	139	$\frac{3}{2}$	Hyp. str.
59	Pr	141	$\frac{3}{2}$	Hyp. str.
75	Re	187	$\frac{3}{2}$	Hyp. str.
	Re	189	$\frac{5}{2}$	
79	Au	197	$\frac{3}{2}$	Hyp. str.
80	Hg	199	$\frac{1}{2}$	Hyp. str.
	Hg	201	$\frac{3}{2}$	
	Hg	198, 200, 202, 204	0	
81	Tl	203	$\frac{3}{2}$	Hyp. str.
	Tl	205	$\frac{5}{2}$	
82	Pb	207	$\frac{1}{2}$	Hyp. str.
	Pb	204, 206, 208	0	
83	Bi	209	$\frac{3}{2}$	Hyp. str.

Many of the values of  $i$  should be accepted with considerable reserve.

the measurements are precise and the interpretation sometimes not easy: while in alternating intensities the theory is beyond doubt, but the difficulty of measurement considerable.

**137. Nuclear spins from atomic and molecular beams.**— Powerful methods for measuring nuclear spins (and also of nuclear magnetic moments) by applications of atomic and molecular beams have been devised and refined by Rabi<sup>1</sup> and his pupils. These methods have given the most reliable results for the nuclear spins of isotopes, and are now giving most important evidence on the quadrupole moments of isotopes, e.g.  $^{69}\text{Ga}$  and  $^{71}\text{Ga}$ .<sup>2</sup>

In Table XX are given some of the nuclear spins measured by the methods which have been described. These data have provided the experimental foundation for attempts to build up nuclear energy terms on the lines of the extra-nuclear electronic energy terms. The first plausible suggestion came from Bartlett,<sup>3</sup> who, making the assumption that only protons contribute to the total nuclear spin, constructed hypothetical proton levels by analogy with familiar electronic levels. Thus he supposed  $^{19}\text{F}$  to have a proton scheme similar to the electronic arrangement in the  $^2\text{S}$  term of potassium. Though the subject cannot be pursued here, it may be said that these energy schemes account for too many facts to be dismissed easily; their theoretical basis, however, remains sketchy. An interesting survey was recently given by Inglis.<sup>4</sup>

<sup>1</sup> Rabi, *Phys. Rev.*, **43**, 236, 1933; Fox and Rabi, *ibid.*, **48**, 746, 1935; Rabi, Millman, Kusch, Zacharias, *ibid.*, **55**, 526, 1939.

<sup>2</sup> Renzetti, *Phys. Rev.*, **57**, 753, 1940.

<sup>3</sup> Bartlett, *ibid.*, **42**, 370, 1932.

<sup>4</sup> Inglis, *ibid.*, **56**, 1175, 1939.

## CHAPTER XVI

### THE SEPARATION OF ISOTOPES

**138. The separation of isotopes.**—The importance, from purely practical and technical points of view, of the theory of isotopes would have been insignificant had its application been confined to the radioactive elements and their products, which are only present in infinitesimal quantities on the Earth. But now that the isotopic nature of the elements in everyday use has been demonstrated, the possibility of their separation, to any reasonable extent, raises questions of some importance to applied science. In physics all constants involving, e.g., the density of mercury or the atomic weight of silver may have to be redefined, while in chemistry reconstruction may be necessary for that part of the science the numerical foundations of which have hitherto rested securely upon the constancy of atomic weights.

It is therefore of great interest to consider in turn the various methods of separation proposed and examine how far they have been successful in practice.

**139. Separation by diffusion.**—The subject of the separation of a mixture of two gases by the method of Atmolysis or Diffusion has been thoroughly investigated by the late Lord Rayleigh.<sup>1</sup> The diffusion is supposed to take place through porous material. The conditions under which maximum separation is to be obtained are that "mixing" is perfect, so that there can be no accumulation of the less diffusible gas at the surface of the porous material, and that the apertures in the material through which the gases must pass are very small compared with the mean free path of the molecules. If these conditions are satisfied he obtains as an expression for the effect of a single operation :

$$\frac{x+y}{X+Y} = \frac{X}{X+Y} r_{\nu-\mu}^{\nu} + \frac{Y}{X+Y} r_{\nu-\mu}^{\mu}$$

where ( $X, Y$ ) ( $x, y$ ) are the initial and final volumes of the gases,  $\mu, \nu$ , the velocities of diffusion, and  $r$  the enrichment of the residue as regards the second constituent.

<sup>1</sup> Rayleigh, *Phil. Mag.*, **42**, 493, 1896.

The velocity of diffusion of a gas is proportional to the square root of the mass of its molecules, so that if a mixture of two isotopes is allowed to diffuse a change in composition *must* be brought about. Now no known isotopes, except those of hydrogen, differ from each other much in mass, so the difference between their rates of diffusion will also be small, hence the above equation may be written in the approximate form—

$\frac{x+y}{X+Y} = r^{\frac{1}{k}}$  where  $k = \frac{\nu - \mu}{\mu}$  a small quantity and, finally, the enrichment by diffusion of the residue as regards the heavier constituent may be expressed with sufficient accuracy by the expression

$$r = \frac{m_2 + m_1}{m_2 - m_1} \sqrt{\frac{\text{Initial volume}}{\text{Final volume}}}$$

where  $m_1$ ,  $m_2$  are the molecular masses of the lighter and heavier isotope respectively. In the case of the isotopes of neon, the number over the root is 21 so that the change in composition obtainable in a single operation will in practice be very small.

If we take the density of the original mixture as unity, the increase in density of the residual gas to be expected from the operation of diffusion will be approximately

$$(r - 1) \times \frac{Y}{X} \times 2 \frac{m_2 - m_1}{m_2 + m_1}$$

Now neon consists of monatomic molecules differing between each other in mass by 10 per cent. and the heavier is present to the extent of 10 per cent. In the diffusion experiments described on p. 35 the effective ratio of the initial volume to the final volume was estimated as certainly greater than 500 and probably less than 10,000, so that  $r$  lies between 1.3 and 1.5. Hence the increase of density of the heavier residue should have been between .003 and .005. It was actually .004.

In the case of other isotopic gaseous mixtures the numerical obstacles in the way of practical separation will be correspondingly greater. Thus in the case of HCl the 36th root is involved, and in that of HBr the 80th root. Although this is compensated to some extent by the larger percentage of the rarer isotope it is clear that the only way by which measurable increase in density may be hoped for will clearly be by increasing very largely the effective ratio of the initial to final volumes. This can be done by experiments on a huge scale or by a vast number of mechanical repetitions.

Harkins started to attack the HCl problem in 1916<sup>1</sup> using the first of these two alternatives. In 1920 he mentions a quantity of

<sup>1</sup> Harkins, *J. Amer. Chem. Soc.*, Feb., 1916.

19,000 litres of HCl as having been dealt with in these experiments.<sup>1</sup> In the following year<sup>2</sup> he published numerical results indicating that a change in atomic weight of 0·055 of a unit had been achieved.

A full account of these operations was published in 1921,<sup>3</sup> and later it was proved that chlorine with an atomic weight as low as 35·418 could be obtained.<sup>4</sup>

In a discussion on isotopes in 1921 Sir J. J. Thomson<sup>5</sup> pointed out that a change in the molecular weight of HCl should be caused by allowing a stream of the gas to flow over the surface of a material which absorbed it. The higher diffusion coefficient of the lighter isotope would result in it being absorbed more rapidly than the heavier one, so that the residue of unabsorbed gas should give a higher molecular weight. This "free diffusion" without the interposition of porous material was exhaustively tried in the Cavendish Laboratory by Ludlam, but without success.<sup>6</sup>

The problem of separation by diffusion was studied systematically by Hertz,<sup>7</sup> who in 1932 was able to announce a spectacular success with neon. Gaseous diffusion through a special porous material at low pressures was employed and by means of an ingenious apparatus requiring no less than 24 mercury diffusion pumps this process was carried out continuously. Starting with normal neon which contains about 9 parts of isotope 20 to 1 part of isotope 22, Hertz was able to produce a light fraction in which the proportion of 22 was reduced below 1 per cent., and a heavy one in which the order was actually reversed and the proportion of 22 greater than that of 20 in the ratio 5 : 2. These fractions correspond to the unprecedented difference in atomic weight of 1·4 of a unit. The changes in the constitution of the fractions was demonstrated by parabola analysis and also by optical methods.

The separation obtained will depend on the number of units used and with a 50 stage apparatus<sup>8</sup> practically pure <sup>22</sup>Ne was prepared. The next improvement introduced was to use the mercury vapour in the pumps as the diffusion medium.<sup>9</sup> In this way the rapidity of the process was much increased.

<sup>1</sup> Harkins, *Science*, Mar. 19, 1920; *Nature*, April 22, 1920; see also *Phys. Rev.*, 15, 74, 1920; *Science*, 51, 289, 1920; *J. Amer. Chem. Soc.*, 42, 1328, 1920.

<sup>2</sup> Harkins, *Science*, Oct. 14, 1921; *Nature*, Oct. 3, 1921.

<sup>3</sup> Harkins and Hayes, *J. Amer. Chem. Soc.*, 43, 1803, 1921.

<sup>4</sup> Harkins and Jenkins, *ibid.*, 48, 58, 1926.

<sup>5</sup> J. J. Thomson, *Proc. Roy. Soc.*, A, 99, 98, 1921.

<sup>6</sup> Ludlam, *Proc. Camb. Phil. Soc.*, 21, 45, 1922.

<sup>7</sup> *Naturwiss.*, 26, 494; *Zeit. Phys.*, 79, 108, 1932.

<sup>8</sup> Harmsen, *Zeit. Phys.*, 82, 589, 1933; 90, 703, 1934.

<sup>9</sup> Hertz, *ibid.*, 91, 810, 1934.

Hertz's method is most successful with inactive gases, not only can specimens of practically pure  $^{20}\text{Ne}$  and  $^{22}\text{Ne}$  be obtained in workable volume, but Kopfermann and Kruger<sup>1</sup> by a run of 300 hours with argon obtained over half a c.c. of gas in which the ratio  $^{36}\text{A}$  to  $^{40}\text{A}$  had been increased from 1 : 330 to 1 : 1. With normal chemically active material it has not been so effective, though some success has been achieved with nitrogen<sup>2</sup> and with methane; <sup>3</sup> owing to the low pressures required the application of separation by simple diffusion on anything like a chemical scale presents great technical difficulties.

**140. Separation by thermal diffusion.**—It has been shown on theoretical grounds independently by Enskog<sup>4</sup> and Chapman<sup>5</sup> that if a mixture of two gases of different molecular weights is allowed to diffuse freely, in a vessel of which the ends are maintained at two different temperatures  $T, T'$ , until equilibrium conditions are reached, there will be a slight excess of the heavier gas at the cold end, and of the lighter gas at the hot end. The separation attained depends on the law of force between the molecules and is a maximum if they behave as elastic spheres. The effect was experimentally verified for a mixture of  $\text{CO}_2$  and  $\text{H}_2$  by Chapman and Dootson,<sup>6</sup> and recently Ibbs<sup>7</sup> has demonstrated that the separation can be carried out continuously and that the time for equilibrium to be established is quite short.

Chapman has suggested<sup>8</sup> that thermal diffusion might be used to separate isotopes. He shows that the separating power depends on a constant  $k_T$ . And when the difference between the molecular masses  $m_1, m_2$  is small the value of this is approximately given by

$$k_T = \frac{17}{3} \frac{m_2 - m_1}{m_2 + m_1} \frac{\lambda_1 \lambda_2}{9.15 - 8.25 \lambda_1 \lambda_2}$$

where  $\lambda_1, \lambda_2$  denote the proportions by volume of each gas in the mixture; thus  $\lambda_1 + \lambda_2 = 1$ . The actual separation is given by

$$\lambda_1 - \lambda'_1 = -(\lambda_1 - \lambda'_2) = k_T \log(T'/T).$$

He gives the following numerical example: "Suppose that it is desired to separate a mixture of equal parts of  $^{20}\text{Ne}$  and  $^{22}\text{Ne}$ , then, writing  $m_1 = 20, m_2 = 22, \lambda_1 = \lambda_2 = \frac{1}{2}$ , we find that  $k_T = 0.0095$ .

<sup>1</sup> Hertz, *Zeit. Phys.*, **105**, 395, 1937.

<sup>2</sup> Woolridge and Jenkins, *Phys. Rev.*, **49**, 704, 1936.

<sup>3</sup> Kruger, *Naturwiss.*, **26**, 445, 1938; Capron, Delfosse, de Hemptinne and Taylor, *J. Chem. Phys.*, **6**, 656, 1938.

<sup>4</sup> Enskog, *Phys. Zeit.*, **12**, 538, 1911; *Ann. Phys.*, **38**, 750, 1912.

<sup>5</sup> Chapman, *Phil. Trans.*, A, **217**, 115, 1916; *Phil. Mag.*, **34**, 146, 1917.

<sup>6</sup> Chapman and Dootson, *ibid.*, **34**, 248, 1917.

<sup>7</sup> Ibbs, *Proc. Roy. Soc.*, A, **99**, 385, 1921.

<sup>8</sup> Chapman, *Phil. Mag.*, **38**, 182, 1919.

Suppose that the mixture is placed in a vessel consisting of two bulbs joined by a tube and one bulb is maintained at  $80^{\circ}$  absolute by liquid air, while the other is heated to  $800^{\circ}$  absolute (or  $527^{\circ}\text{C}.$ ). When the steady state has been attained the difference of relative concentration between the two bulbs is given by the equation

$$\lambda_1 - \lambda'_1 = -(\lambda_2 - \lambda'_2) = 0.0095 \log, 800/80 \\ = 0.022$$

or 2.2 per cent. Thus the cold bulb would contain 48.9 per cent.  $^{20}\text{Ne}$  to 51.1 per cent.  $^{22}\text{Ne}$ , and vice versa in the hot bulb. By drawing off the contents of each bulb separately, and by repeating the process with each portion of the gas, the difference of relative concentrations can be much increased. But as the proportions of the two gases become more unequal, the separation effected at each operation slowly decreases. For instance, when the proportions are as 3 : 1, the variation at each operation falls to 1.8 per cent.; while if they are as 10 : 1 the value is 1.2 per cent. This assumes that the molecules behave like elastic spheres: if they behave like point centres of force varying as the inverse  $n$ th power of the distance, the separation is rather less; e.g., if  $n = 9$ , it is just over half the above quantities."

Chapman points out that for equal values of  $\log (p'/p)$  and  $\log (T'/T)$  pressure diffusion (centrifuging) is about three times as powerful as thermal diffusion but suggests that it may be more convenient to maintain large differences of temperature than of pressure.

Thermal diffusion as a means of isotope separation was suddenly raised from an interesting theoretical possibility to a method of outstanding practical importance by the recent sensational discovery by Clausius and Dickel<sup>1</sup> that in a system consisting simply of a long vertical hot wire in a cooled cylinder the convection currents, naturally set up, instead of hindering actually assist, to an almost incredible degree, the operation of separating the lighter from the heavier molecules. The former accumulate at the top of the cylinder and the latter at its base. The operation can be carried out at ordinary atmospheric pressure and the longer the cylinder the more perfect the separation when equilibrium occurs. In their first report they showed that with a temperature difference of about  $600^{\circ}$  large changes in the composition of neon were brought about. In their second<sup>2</sup> a tube 30 metres long was described by which, by the use of gaseous HCl, an unprecedented separation of the isotopes of chlorine was achieved.

Even this performance was improved upon, and samples of chlorine in quantity were prepared which when analysed by Honigschmid and

<sup>1</sup> *Naturwiss.*, 26, 546, 1938.

<sup>2</sup> *Ibid.*, 27, 148, 1939.

Hirschbold-Wittner<sup>1</sup> gave chemical atomic weights 34.971 and 36.968, practically 100 per cent. separation, a most remarkable achievement. This form of thermal diffusion is clearly one of the most promising methods of separation on a large scale. A very complete theoretical analysis of the process has been given by Furry, Clark-Jones and Onsager,<sup>2</sup> and a discussion on the optimal dimensions of the apparatus by Krasny-Ergen.<sup>3</sup>

**141. Separation by gravitation or "pressure diffusion."**—When a heterogeneous fluid is subjected to a gravitational field its heavier particles tend to concentrate in the direction of the field, and if there is no mixing to counteract this a certain amount of separation must take place. If therefore we have a mixture of isotopes in a gaseous or liquid state partial separation should be possible by gravity or centrifuging.

The simplest case to consider is that of the isotopes of neon in the atmosphere and, before the matter had been settled by the mass spectrograph, analysis of the neon in the air at very great heights was suggested as a possible means of proving its isotopic constitution.<sup>4</sup> The reasoning is as follows:

If  $M$  be the atomic weight,  $g$  the gravitational constant,  $p$  the pressure, and  $\rho$  the density, then if no mixing takes place  $dp = -g\rho dh$ ,  $h$  being the height. In the isothermal layer convection is small. If it is small compared with diffusion the gases will separate to a certain extent. Since  $T$  is constant

$$p = \frac{RT\rho}{M} \text{ and } \frac{d\rho}{\rho} = \frac{M\rho}{RT} dh,$$

$$\text{whence } \rho = \rho_0 e^{-\frac{Mg}{RT} \Delta H},$$

$\rho_0$  being the density at the height  $h_0$  at which mixing by convection ceases, about 10 kilometres, and  $\Delta h$  the height above this level. If two isotopes are present in the ratio 1 to  $K_0$ , so that the density of one is  $\rho_0$  and of the other  $K_0\rho_0$  at height  $h_0$ , then their relative density at height  $h_0 + \Delta h$  is given by

$$K = K_0 e^{-\frac{g\Delta h}{RT}(M_1 - M_2)}.$$

Putting  $T = 220$  as is approximately true in England,

$$\frac{K}{K_0} = e^{-5.38 \times 10^{-3} \Delta h (M_1 - M_2)},$$

<sup>1</sup> *Zeit. Anorg. Chem.*, **242**, 222, 1939.

<sup>2</sup> *Phys. Rev.*, **55**, 1083, 1939.

<sup>3</sup> *Ibid.*, **58**, 1078, 1940.

<sup>4</sup> Lindemann and Aston, *Phil. Mag.*, **37**, 530, 1919.

$\Delta h$  being measured in kilometres. If  $M_1 - M_2 = 2$ , therefore

$$\frac{K}{K_0} = e^{-\frac{\Delta h}{R}}$$

It might be possible to design a balloon which would rise to 100,000 feet and there fill itself with air. In this case the relative quantity of the heavier constituent would be reduced from 10 per cent. to about 8·15, so that the atomic weight of neon from this height should be 20·163 instead of 20·2. If one could get air from 200,000 feet, e.g. by means of a long-range gun firing vertically upwards, the atomic weight of the neon should be 20·12.

A more practicable method is to make use of the enormous gravitational fields produced by a high-speed centrifuge.

In this case the same equation holds as above except that  $g$  varies from the centre to the edge. In a gas therefore

$$\frac{d\rho}{\rho} = - \frac{Mv^2 dr}{RT \cdot r} = - \frac{M\omega^2}{RT} r dr,$$

whence

$$\rho = \rho_0 e^{-\frac{M\omega^2}{2RT} r^2}$$

$v_0$  being the peripheral velocity. Here again, if  $K_0$  is the ratio of the quantities present at the centre, the ratio at the edge will be

A peripheral velocity of  $10^5$  cm./sec. or perhaps even  $1\cdot3 \times 10^5$  cm./sec. might probably be attained in a specially designed centrifuge,

so that  $\frac{K}{K_0}$  might be made as great as  $e^{-0\cdot205(M_1-M_2)}$  or even  $e^{-0\cdot37(M_1-M_2)}$ .

If  $M_1 - M_2$  is taken as 2 a single operation would therefore give fractions with a change of  $K$  of 0·65. In the case of neon the apparent atomic weight of gas from the edge would be about 0·65 per cent. greater than that of gas from the centre, i.e. a separation as great as the best yet achieved in practice by any method could be achieved in one operation. By centrifuging several times or by operating at a lower temperature the enrichment might be increased exponentially.

Centrifuging a liquid, e.g. liquid lead, would not appear so favourable, though it is difficult to form an accurate idea of the quantities without a knowledge of the equation of state. If compression is neglected and the one lead treated as a solution in the other, a similar formula to that given above holds. On assumptions similar to these Poole<sup>1</sup> has calculated that a centrifuge working with a peripheral velocity of about  $10^4$  cm./sec. should separate the isotopes of mercury to an extent corresponding to a change of density of 0·000015.

The first experiments on the separation of isotopes by the use of

<sup>1</sup> Poole, *Phil. Mag.*, 41, 818, 1921.

a centrifuge are those of Joly and Poole<sup>1</sup> who attempted to separate the hypothetical isotopic constituents of ordinary lead by this means. No positive results were obtained and the check experiments made with definite alloys of lighter metals with lead were by no means encouraging.

Mulliken<sup>2</sup> gives a complete theory of the separation of isotopes by thermal diffusion and by centrifuging, and shows that the latter method is likely to be of more value in the case of isotopes of high atomic weight. A special method, named evaporative centrifuging, is proposed whereby gas condensed in the periphery of the centrifuge at high speed would be allowed to evaporate very slowly, the light fractions being drawn off very gradually at low pressure from the centre of the apparatus. It is suggested that this method ought to yield a separation 10 to 15 times as great in one operation as would diffusion or evaporation. He also discusses the possibility of separating liquid isotopes by centrifuging. An attempt to test this theory in the case of mercury proved unsuccessful, and its failure is attributed to slight vibration of the centrifuge.

The recent advances in the design of centrifuges, particularly of the ultra-rapid air-driven types have led to further trials of the method by Beams and his co-workers, who worked with  $\text{CCl}_4$ . They report that the density changes produced are in agreement with theory, and consider the method a promising one.<sup>3</sup>

**142. Separation by chemical action or ordinary fractional distillation.**—The possibility of separating isotopes by means of the difference between their chemical affinities or vapour pressures has been investigated fully from the theoretical standpoint by Lindemann. The thermodynamical considerations involved are the same in both cases. The reader is referred to the original papers<sup>4</sup> for the details of the reasoning by which the following conclusion is reached :

"Isotopes must in principle be separable both by fractionation and by chemical means. The amount of separation to be expected depends upon the way the chemical constant is calculated and upon whether 'Nullpunkttsenergie' is assumed. At temperatures large compared with  $\beta\nu$ ,<sup>5</sup> which are the only practicable temperatures as far as lead is concerned, the difference of the vapour pressure and the constant of the laws of mass action may be expanded in powers of  $\beta\nu/T$ . The most important term of the type  $\log (\beta\nu/T)$  is can-

<sup>1</sup> Joly and Poole, *ibid.*, 39, 372, 1920.

<sup>2</sup> Mulliken, *J. Amer. Chem. Soc.*, 44, 1033, 1922; 45, 1592, 1923.

<sup>3</sup> *J. Chem. Phys.*, 5, 993, 1937.

<sup>4</sup> Lindemann, *Phil. Mag.*, 37, 523, 1919; 38, 173, 1919.

<sup>5</sup>  $\beta\nu$  is the "characteristic" and T the "Absolute" temperature.

celled by the chemical constant if this is calculated by what seems the only reasonable way. The next term in  $(\beta\nu/T)$  is cancelled by the 'Nullpunktsenergie' if this exists. All that remains are terms containing the higher powers of  $\beta\nu/T$ . In practice therefore fractionation does not appear to hold out prospects of success unless one of the above assumptions is wrong. If the first is wrong a difference of as much as 3 per cent. should occur at  $1200^\circ$  and a difference of electromotive force of one millivolt might be expected. Negative results would seem to indicate that both assumptions are right."

The negative result of the laborious efforts to separate the isotopes of neon by fractionation over charcoal cooled in liquid air has already been recounted.<sup>1</sup> On the other hand, more recently Keesom and van Dijk<sup>2</sup> have investigated the possibility of separating the isotopes of neon by rectification at or near its triple point. The vapour pressure curve for mixtures of isotopes as a function of composition calculated by Stern (not published) suggested that separation was practicable by this means. Using an elaborate rectifying column and distilling at  $-248.4^\circ C.$  they succeeded in obtaining light and heavy fractions of densities corresponding to atomic weights 20.14 and 20.23 respectively, ordinary neon being taken as 20.18. They consider that these results satisfy the theory reasonably well and prove to a high degree of probability the very important conclusion that the solid state possesses zero-point energy. Continuing this work<sup>3</sup> they improved their results to a remarkable degree, obtaining fractions of neon having an atomic weight as high as 21.157. This separation is, of course, not so great as that obtained by Hertz<sup>4</sup> but the quantities dealt with are much more considerable.

Evaporation near the triple point was used by Urey, Brickwedde and Murphy<sup>5</sup> to concentrate deuterium to a point at which it was detected spectroscopically. Since that discovery much work has been done on the fractional distillation of water, not only to increase the deuterium content, but also that of the heavier isotopes of oxygen.<sup>6</sup> As the efficiency of the process is very low elaborate stills must be used and the concentrates so made show very small increases in density, but owing to the extreme delicacy possible in density measurements they are of value in the study of exchange reactions. Similar attempts to concentrate heavy nitrogen by the distillation of ammonia have not met with much success.<sup>7</sup>

<sup>1</sup> V. p. 33.

<sup>2</sup> Proc. Roy. Acad. Amst., 34, 42; 1931.

<sup>3</sup> Ibid., 37, 615, 1934; 38, 809, 1935.

<sup>4</sup> V. p. 246.

<sup>5</sup> Phys. Rev., 39, 164; 40, 1, 1932.

<sup>6</sup> Lewis and Cornish, J. Amer. Chem. Soc., 55, 2616, 1933; Wahl and Urey, J. Chem. Phys., 3, 411, 1935; Huffman and Urey, Ind. Eng. Chem., 29, 531, 1937.

<sup>7</sup> Wahl, Huffman and Hippel, J. Chem. Phys., 3, 434, 1935.

**143. Separation by chemical exchange methods.**—As was recounted in Chapter II the most careful chemical analysis, assisted by radioactive methods of extraordinary delicacy, was unable to achieve the slightest separation of radioactive isotopes. Results with stable elements known to be complex were for a long period equally negative. Thus the report that the isotopes of lead could be separated by means of the Grignard reaction proved to be unfounded,<sup>1</sup> and King<sup>2</sup> made careful and exhaustive attempts to separate the isotopes of mercury by chemical means. Six different reactions were studied but no separation was detected.

Knowledge of the mechanism of exchange reactions was much advanced by the discovery and use of deuterium which could be compared with protium in its reactions, and it was shown that similar differences, though smaller numerically, might be employed to separate the isotopes of other elements. Urey and Greiff<sup>3</sup> gave a general discussion on isotopic exchange equilibria, indicating those which offered the most hopeful means of enriching the abundance of the heavier isotopes of carbon, nitrogen and oxygen. The problem is similar to that of separation by fractional distillation, and counter-current flows in packed fractionating columns are employed.

For the concentration of  $^{13}\text{C}$  the most efficient reaction appears to be that between HCN gas and a solution of NaCN in water. By this means NaCN containing 25 atoms per cent.  $^{13}\text{C}$  has been produced at the rate of 2.5 gr. per day.<sup>4</sup> For nitrogen various ammonia reactions were studied and that between ammonia and ammonium nitrate yielded a sample containing as much as 14.5 per cent. heavy nitrogen.<sup>5</sup> An even better result was obtained later by a special counter-current flow distillation column apparatus<sup>6</sup> which is claimed to have an efficiency 1000 times that of the Hertz cascade diffusion method, and a final concentration of 72.8 per cent.  $^{15}\text{N}$  was reported. In similar work by Stewart and Cohen<sup>7</sup> on the reaction of  $\text{SO}_2$  gas on sodium bisulphite solution a yield of 3.2 grs. per day of S containing 25 per cent.  $^{34}\text{S}$  was obtained.

Another mechanism for making use of exchange reactions is that of the liquid-solid system in which alkali metal ions are absorbed and exchanged in zeolites. If a solution of lithium chloride is allowed to descend a column containing sodium zeolite the isotopes of the lithium replace the atoms of sodium at a slightly different rate, and a similar

<sup>1</sup> Brennen, *Compt. Rend.*, **180**, 282, 1925; Richards, King and Hall, *J. Amer. Chem. Soc.*, **48**, 1530, 1926.

<sup>2</sup> *Ibid.*, **49**, 1500, 1927.

<sup>3</sup> *Ibid.*, **57**, 321, 1935.

<sup>4</sup> Hutchinson, Stewart and Urey, *J. Chem. Phys.*, **8**, 532, 1940.

<sup>5</sup> Thode, Gorham and Urey, *ibid.*, **6**, 296, 1938.

<sup>6</sup> Thode and Urey, *ibid.*, **7**, 34, 1939.

<sup>7</sup> *Ibid.*, **8**, 904, 1940.

difference is shown in the reverse reaction. These effects are small but by the use of a very long 100-foot column Taylor<sup>1</sup> claims to have changed the isotope ratio in lithium to some extent.

**144. Separation by evaporation at very low pressure.**—If a liquid consisting of isotopes of different mass is allowed to evaporate it can be shown that the number of light atoms escaping from the surface in a given time will be greater than the number of heavier atoms in inverse proportion to the square roots of their weights. If the pressure above the surface is kept so low that none of these atoms return, the concentration of the heavier atoms in the residue will steadily increase. This method has been used for the separation of isotopes by Brönsted and Hevesy, who applied it first to the element mercury.

The mercury was allowed to evaporate at temperatures from 40° to 60° C. in the highest vacuum attainable. The evaporating and condensing surfaces were only 1 to 2 cm. apart, the latter was cooled in liquid air so that all atoms escaping reached it without collision and there condensed in the solid form.

It will be seen that the liquid surface acts exactly like the porous diaphragm in the diffusion of gases.<sup>2</sup> The diffusion rate of mercury can be obtained approximately from the diffusion rate of lead in mercury<sup>3</sup> and is such that the mean displacement of the mercury molecule in liquid mercury is about  $5 \times 10^{-3}$  cm. sec.<sup>-1</sup>. It follows that if not more than  $5 \times 10^{-3}$  c.c.m. per cm.<sup>2</sup> surface evaporates during one second no disturbing accumulation of the heavier isotope in the surface layer takes place.

The separation was measured by density determination. Mercury is particularly well suited for this and a notable feature of this work was the delicacy with which it could be performed. With a 5-c.c.m. pyknometer an accuracy of 1 part in 2,000,000 is claimed. The first figures published<sup>4</sup> were :

Condensed mercury . . . . .	0.999981
Residual mercury . . . . .	1.000031

the densities being referred to ordinary mercury as unity.

The later work was on a larger scale.<sup>5</sup> 2700 c.c.m. of mercury were employed and fractionated systematically to about 1/100,000 of its original volume in each direction. The final figures were :

Lightest fraction vol. 0.2 c.c. .	0.99974
Heaviest fraction vol. 0.3 c.c. .	1.00023

<sup>1</sup> *Science*, **89**, 176, 1939.

<sup>2</sup> *V.* p. 244.

<sup>3</sup> Groh and Hevesy, *Ann. Physik.*, **63**, 92, 1920.

<sup>4</sup> Brönsted and Hevesy, *Nature*, Sept. 30, 1920.

<sup>5</sup> *Ibid., Phil. Mag.*, **43**, 31, 1922.

Mercury behaves as though it was a mixture of equal parts of two isotopes with atomic weights 202·0, 199·2 in equal parts or of isotopes 201·3, 199·8 when the former is four times as strong as the latter, and so on. These figures correspond to an isotopic moment of 1·40, in exact agreement with the result obtained by photometry of the mass spectrum.<sup>1</sup>

Honigschmid and Birckenbach<sup>2</sup> have examined the chemical atomic weight of samples of mercury of different density obtained by the method of Brönsted and Hevesy with the following results :

	Density.	Atomic Weight.
Lightest fraction . . .	0·999824	$200\cdot564 \pm 0\cdot006$
Ordinary mercury . . .	1·000000	$200\cdot61 \pm 0\cdot006$
Heaviest fraction . . .	1·000164	$200\cdot632 \pm 0\cdot007$

The separation of the isotopes of mercury by this and analogous processes has been systematically studied by Mulliken.<sup>3</sup> Harkins and Madorsky<sup>4</sup> describe a steel apparatus in which 2·5 kilograms of mercury can be dealt with in one operation. The mercury is contained in an annular trough surmounted by a Λ-shaped condensing surface. The latter is cooled with ice so that the fractions can be drawn off continuously without interrupting the distillation and the use of liquid air is eliminated. After 268 hours of operation with the large apparatus and 37 hours with a smaller glass one, they obtained a light fraction of 3·8 grs. of mercury, showing a decrease in atomic weight of 0·044 of a unit, and a heavy fraction of 4·4 grs. showing an increase of 0·052 of a unit.

This work has since been extended by Harkins and Mortimer.<sup>5</sup> By means of still further technical improvements enabling increased speed of fractionation they have obtained two samples of mercury of about 100 grammes each which show a total difference of density corresponding to 0·189 of a unit of atomic weight.

**145. Separation of the isotopes of chlorine by free evaporation.**—Brönsted and Hevesy were able to announce the first separation of the isotopes of chlorine<sup>6</sup> by applying the above method to a solution of HCl in water. This was allowed to evaporate at a temperature of  $-50^\circ\text{C}$ . and condense on a surface cooled in liquid

<sup>1</sup> Aston, *Proc. Roy. Soc., A*, **126**, 511, 1930.

<sup>2</sup> Honigschmid and Birckenbach, *Ber.*, **56**, 1219, 1923.

<sup>3</sup> Mulliken, *J. Amer. Chem. Soc.*, **44**, 2387; **45**, 1592, 1923.

<sup>4</sup> Harkins and Madorsky, *Nature*, **111**, 148, 1923; *J. Amer. Chem. Soc.*, **45**, 591, 1923.

<sup>5</sup> Harkins and Mortimer, *Phil. Mag.*, **6**, 601, 1928.

<sup>6</sup> Brönsted and Hevesy, *Nature*, July 14, 1921.

air. Starting with 1 litre 8.6 mol. solution of HCl 100 c.c. each of the lightest and heaviest fraction were obtained.

The degree of separation achieved was tested by two different methods. In the first the density of a saturated solution of NaCl made from the distillate and the residue respectively was determined with the following results :

$$\text{Density (salt from distillate)} = 1.20222$$

$$\text{Density (salt from residue)} = 1.20235$$

These figures correspond to a change in atomic weight of 0.024 of a unit.

In the second method exactly equal weights of the isotopic sodium chlorides were taken and each precipitated with accurately the same volume of AgNO<sub>3</sub> solution, in slight excess. After precipitation and dilution to 2000 c.c. the approximate concentration of the filtrate was determined by titration, also the ratio of Ag concentration of the two solutions was measured in a concentration cell. Calculation showed that the difference in atomic weight of the two samples was 0.021, in good agreement with the density result.

**146. Experiments on zinc and other elements.**—Experiments on the separation of the isotopes of zinc have been made by Egerton and Lee<sup>1</sup> using the free evaporation method. In order to detect separation the densities of the end fractions were determined in the solid state. For this purpose they were cast in a vacuum and seeded with about 1 mg. of a particular kind of zinc. The first set of distillations gave a residue of slightly increased density, but the distillate was of the same density as the original zinc. The second set of distillations carried out under improved conditions yielded a residue showing a density increased by about 1 part in 3700 and a distillate of a density decreased by about 1 part in 3600. They discuss the possibility of attributing the difference of density to flaws, different physical conditions, or impurities, and show this to be unlikely.

With the isotopes of lead the method has not been so effective. Brönsted and Hevesy distilled lead chloride in a high vacuum. The end fractions were then submitted to atomic weight determinations by Honigschmid and Steinheil.<sup>2</sup> The results were 207.229 and 207.236, a difference too small in their opinion to warrant any claim for separation. A similar negative result has been recorded for the distillation of cadmium,<sup>3</sup> ordinary lead, and a mixture of ordinary lead and uranium lead.<sup>4</sup>

<sup>1</sup> Proc. Roy. Soc., A., 103, 499, 1923.

<sup>2</sup> Ber., 56, 1931, 1923.

<sup>3</sup> Sunier, Abs. Theses., Univ., Chicago, 4, 173, 1925-26.

<sup>4</sup> Richards, King and Hall, J. Amer. Chem. Soc., 48, 1530, 1926.

The method was applied in an elegant manner by Hevesy and Logstrup<sup>1</sup> to the interesting problem of the radioactivity of potassium. The pure metal was subjected to a prolonged series of fractionations at the end of which the atomic weight of the heaviest fraction was determined by Honigschmid and Goubeau to be 0.005 of a unit higher than that of ordinary potassium. Measurements of the radioactivity of this fraction showed that this property followed exactly the change in the percentage of the heavier isotope present. As potassium consists of isotopes 39 and 41 it was therefore to be concluded that the radioactivity was confined to 41 or some other unknown isotope heavier than 39. This conclusion has now been verified by the discovery and isolation of the radioactive isotope of mass number 40.<sup>2</sup>

**147. Separation by mass ray analysis.**—An obvious method of separating isotopes completely and obtaining pure specimens of the constituents of a complex element is by analysing a beam of its ions and trapping the particles sorted out in different vessels. The typical case of the parabola analysis of neon was considered by the writer<sup>3</sup> and it was shown that with the ordinary gaseous discharge, even under the most favourable conditions, the quantities produced would be exceedingly small, of the order 0.1 cubic millimetre for a 100-seconds run.

Anode rays held out more hope and an apparatus designed to produce specimens of pure isotopes 6 and 7 of lithium was described by Morand.<sup>4</sup> He used an anode of heated lithium salt, but although valuable estimates of the relative abundance of the isotopes were obtained no success with the original problem was reported.

Some years later, following the discovery of artificial disintegration, the great importance of obtaining, for bombardment, targets of pure isotopes was realized, and also that for this particular purpose the quantities required were microscopic. The problem was successfully attacked in America and England in the same year. In California Smythe, Rumbaugh and West<sup>5</sup> by means of a high-intensity spectrometer using a special type of magnetic focusing, were able to separate and concentrate the anode rays of potassium. Using a Kunsman catalyst<sup>6</sup> and a considerable area of anode they produced as much as 1 mg. of  $^{39}\text{K}$  in a seven hours' run. Small quantities of  $^6\text{Li}$  and  $^7\text{Li}$  were also prepared as disintegration targets. At the Cavendish Laboratory Oliphant, Shire and Crowther<sup>7</sup> used a simple

<sup>1</sup> *Nature*, **120**, 838, 1927.

<sup>2</sup> V. p. 144.

<sup>3</sup> Aston, *Isotopes*, p. 136, 1922.

<sup>4</sup> *Compt. Rend.*, **182**, 460, 1926; *Ann. Physique*, **7**, 164, 1927.

<sup>5</sup> *Phys. Rev.*, **45**, 724, 1934.

<sup>6</sup> V. p. 72.

<sup>7</sup> *Proc. Roy. Soc., A*, **146**, 922, 1934.

type of crossed field analysis apparatus, and a beam of rays from a source containing a lithium salt, alumina and silica heated on a platinum filament. In this way they prepared targets of pure  $^6\text{Li}$  and  $^7\text{Li}$  containing quantities of the order of  $10^{-8}$  gr. which were used with success in disintegration research.

The high-intensity mass spectrometer was later used by Smythe and Hemmendinger<sup>1</sup> to separate all the isotopes of potassium, 39, 40 and 41, and in this way they were able to prove that of them only  $^{40}\text{K}$  was responsible for the radioactivity of the element. By increasing the resolving power they separated the two isotopes of rubidium<sup>2</sup> showing that  $^{87}\text{Rb}$  alone was radioactive. Rubidium was also investigated by Walcher,<sup>3</sup> who isolated enough of the pure isotopes to be able to study their hyper-fine structure spectroscopically.

Yates<sup>4</sup> by using a modification of the apparatus of Oliphant produced pure targets from lithium, 6 and 7, boron, 10 and 11, and carbon, 12, which were used for the work on disintegration at the Cavendish Laboratory. As a source of the boron ions he used a low voltage arc in a mixture of helium and boron trifluoride, and for those of carbon, helium and heavy methane  $\text{CD}_4$ .

The most recent success with mass spectrometer separation is the spectacular one of the isolation of the isotopes of uranium already noted on p. 190.

**148. Separation by photochemical methods.**—An ingenious suggestion was made by Merton and Hartley soon after the discovery of the isotopes of chlorine that their separation might be effected by the following device. Light falling on a mixture of chlorine and hydrogen causes these gases to combine to form hydrochloric acid. This must be due to the activation of the atoms of hydrogen or those of chlorine. Supposing it to be the latter, it is conceivable that the radiation frequency necessary to activate the atoms of  $^{35}\text{Cl}$  will not be quite the same as that necessary to activate those of  $^{37}\text{Cl}$ . Calling these frequencies  $\nu_{35}$  and  $\nu_{37}$ , respectively it would seem possible, by excluding one of these frequencies entirely from the activating beam, to cause only one type of chlorine to combine and so to produce pure  $\text{H}^{35}\text{Cl}$  or  $\text{H}^{37}\text{Cl}$ . Now ordinary chlorine contains about 3 times as much  $^{35}\text{Cl}$  as  $^{37}\text{Cl}$  and these isotopes must absorb their own activating radiation selectively. In this gas therefore light of frequency  $\nu_{35}$  will be absorbed much more rapidly than that of frequency  $\nu_{37}$ , so that if we allow the activating beam to pass through the right amount of chlorine gas  $\nu_{35}$ , might be completely absorbed but sufficient  $\nu_{37}$  radiation transmitted to cause reaction. On certain theories of photo-

<sup>1</sup> *Phys. Rev.*, **51**, 178, 1937.

<sup>3</sup> *Zeit. Phys.*, **108**, 376, 1938.

<sup>2</sup> *Ibid.*, **51**, 1052, 1937.

<sup>4</sup> *Proc. Roy. Soc., A*, **168**, 148, 1938.

chemistry light containing  $\nu_{37}$ , but no  $\nu_{35}$  would cause only atoms of  $^{37}\text{Cl}$  to combine so that a pure preparation of  $\text{H}^{37}\text{Cl}$  would result. Pure  $^{37}\text{Cl}$  made from this product could now be used as a filter for the preparation of pure  $\text{H}^{35}\text{Cl}$ , and this in its turn would yield pure  $^{35}\text{Cl}$  which could then be used as a more efficient filter for the formation of more  $\text{H}^{37}\text{Cl}$ . Unfortunately the results of experiments on this method proved negative.<sup>1</sup>

A somewhat similar photochemical method has been applied recently by Kuhn and Martin.<sup>2</sup> Filtered light corresponding to 2816.179 Å the shortest and strongest component of  $\text{CO}^{35}\text{Cl}^{35}\text{Cl}$  was allowed to fall upon a stream of  $\text{COCl}_2$  vapour mixed with iodine. The chlorine resulting from the photochemical dissociation was caught with  $\text{HgI}_2$  and its atomic weight determined. Two experiments gave 35.428 and 35.430 respectively. A control with ordinary light gave 35.455. The difference corresponds to about one-fifth of the theoretical.

A method suggested by Mrozowski depending on differential absorption of the resonance line 2537 Å by the isotopes of mercury in a magnetic field has been applied by Zuber<sup>3</sup> who claims that by this means the abundance of the mass numbers 200 and 202 was modified by a factor of 4.

**149. Separation by ionic migration.**—It was first suggested by Lindemann<sup>4</sup> that if isotopic ions were allowed to migrate freely through a substance like gelatine, the head of the migrating column might be expected to contain a preponderance of the lighter isotope. Experiments on these lines have been undertaken by several observers, but so far without success. In the experiments of Kendall and Crittenden<sup>5</sup> the conditions were so arranged that the ions moved in an agar-agar gel at the rate of 12 to 18 inches a day. Quantitative separation of sodium iodide from sodium thiocyanate was obtained after a movement of only a few feet, but there was no indication of any separation in the case of sodium chloride even after a movement of 100 feet. Murmann<sup>6</sup> describes many attempts to separate isotopes by this and other methods. All gave negative results and he concludes that ionic mobilities are dependent only on atomic volume and not on atomic weight.

A method which may be considered to depend upon the difference in the electrode potentials of isotopes is that used by Lewis and

<sup>1</sup> *Phil. Mag.*, **43**, 430, 1922.

<sup>2</sup> Kuhn and Martin, *Naturwiss.*, **42**, 772, 1932.

<sup>3</sup> *Nature*, **136**, 796, 1935.

<sup>4</sup> Lindemann, *Proc. Roy. Soc., A*, **99**, 103, 1921; Pilley, *Nature*, **111**, 848, 1923.

<sup>5</sup> Kendall and Crittenden, *Proc. Nat. Acad. Sci.*, **9**, 75, 1923.

<sup>6</sup> Murmann, *Oesterr. Chem. Ztg.*, **26**, 14, 1923.

Macdonald<sup>1</sup> who allowed lithium amalgam to fall in the form of fine drops through a solution of a lithium salt contained in a long column. They found that the lighter isotope was carried preferentially by the amalgam and tended to accumulate at the foot of the column. The experiments were on a large scale, over a ton of amalgam being employed. Under the most favourable conditions the abundance of  $^6\text{Li}$  relative to  $^7\text{Li}$  was approximately doubled and the atomic weight reduced from 6.940 to 6.855.

**150. Separation by electrolysis.**—The possibility of this method was first considered by Kendall and Crittenden,<sup>2</sup> but no positive results were recorded until the discovery of the isotopes of hydrogen, to separate which it was first applied by Washburn and Urey<sup>3</sup> and then by Lewis<sup>4</sup> with the well-known sensational results. Pure heavy water  $\text{D}_2\text{O}$ , made by electrolysis at localities where electric power is cheap, is now an ordinary article of commerce. Some idea of the scale of these operations has already been given on p. 120.

While in hydrogen the conditions for electrolytic separation are exceptionally favourable, with other elements this is not so, though Taylor and Urey<sup>5</sup> by electrolysis of a solution of lithium hydroxide were able to reduce the abundance of  $^6\text{Li}$  in the residue by an appreciable amount. Holleck<sup>6</sup> by continuous electrolysis of a solution of lithium chloride succeeded in changing its atomic weight from 6.941 to 6.894.

With other elements electrolysis appears very ineffective. Kendall<sup>7</sup> failed with mercury, and in the case of oxygen Johnston<sup>8</sup> working on the factor of electrolytic separation of  $^{18}\text{O}$  from  $^{16}\text{O}$  concludes that "reduction of the entire ocean by electrolysis to a residual cubic millimetre would less than double the concentration of the heavy isotopes of oxygen."

**151. Other methods of separation and general conclusions.**—Other methods tried without success are the action of light on metallic chlorides<sup>9</sup> and fractional crystallization.<sup>10</sup>

The partial separation of isotopes has recently acquired greatly increased importance by the use of the so-called "tracer" elements, a device with which the work of Urey is associated. This is an exten-

<sup>1</sup> *J. Amer. Chem. Soc.*, **58**, 2519, 1936.

<sup>2</sup> *Proc. Nat. Acad. Sci.*, **9**, 75, 1923. <sup>3</sup> *Ibid.*, **18**, 496, 1932.

<sup>4</sup> *J. Amer. Chem. Soc.*, **55**, 1297, 1933. <sup>5</sup> *J. Chem. Phys.*, **5**, 597, 1937.

<sup>6</sup> *Zeit. Electrochem.*, **44**, 111, 1938.

<sup>7</sup> *Proc. Roy. Soc. Edin.*, **57**, 182, 1937.

<sup>8</sup> *J. Amer. Chem. Soc.*, **57**, 484, 1935.

<sup>9</sup> Renz, *Zeit. Anorg. Chem.*, **116**, 62, 1921.

<sup>10</sup> Atkinson, *Nature*, **112**, 283, 1923; Robinson and Briscoe, *J. Chem. Soc.*, **127**, 138, 1925.

sion of the idea of indicators, described on p. 17, to the non-radioactive elements, particularly those taking part in biochemical reactions. If the isotopic constitution of, for instance, nitrogen is changed, the heavy element produced can be traced in its reactions by its physical properties, which give means of its recognition quite definite though of course with nothing like the delicacy of radioactivity. To be of practical value considerable quantities are required, but the actual separation necessary is not large and samples of heavy carbon, nitrogen and oxygen have already been put to good use in this remarkable new field of chemistry.

In conclusion it may be stated that although progress in separation of isotopes was slow at first, yet in the last ten years improvement in methods has been so rapid that it would be rash to set bounds to its possible future achievements. It seems probable that while the vast bulk of ordinary chemical operations, performed with naturally occurring substances, will be unaffected, the availability of elements modified artificially by separation has put a new and very powerful tool into the hands of the research worker.

## APPENDIX I

TABLE OF ISOTOPES AND THEIR PERCENTAGE ABUNDANCE

Figures for abundance in ordinary type indicate some form of direct measurement, though their accuracy varies widely as is suggested by the number of digits quoted. Italics indicate rough estimates or indirect calculations from chemical atomic weights. w = weak isotope abundance not determined. Numbers in brackets are doubtful. The figures for abundance are those adopted in the International Table of Stable Isotopes for 1940, with the exception of helium, nickel and molybdenum for which later and more reliable values are given.

Symbol	Atomic Number (Z)	Mass Number (A)	Relative Abundance (%)	Symbol	Atomic Number (Z)	Mass Number (A)	Relative Abundance (%)
H	1	1	99.98	Si	14	28	89.6
D		2	0.02			29	6.2
						30	4.2
He	2	3	$10^{-7}$	P	15	31	100
		4	100	S	16	32	95.1
Li	3	6	7.5			33	0.74
		7	92.5			34	4.2
Be	4	9	100			(36)	(0.016)
B	5	10	20	Cl	17	35	75.4
		11	80			37	24.6
C	6	12	98.9	A	18	36	0.31
		13	1.1			38	0.06
N	7	14	99.62	K	19	39	93.4
		15	0.38			40	0.01
O	8	16	99.76			41	6.6
		17	0.04	Ca	20	40	96.97
		18	0.20			42	0.64
F	9	19	100			43	0.145
Ne	10	20	90.00			44	2.06
		21	0.27			46	0.0033
		22	9.73			48	0.185
Na	11	23	100	Sc	21	45	100
Mg	12	24	77.4	Ti	22	46	7.94
		25	11.5			47	7.75
		26	11.1			48	73.45
Al	13	27	100			49	5.52
				V	23	50	5.34
						51	100

## APPENDIX I

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Symbol	Atomic Number (Z)	Mass Number (A)	Relative Abundance (%)	Symbol	Atomic Number (Z)	Mass Number (A)	Relative Abundance (%)
Cr	24	50	4.49	Rb	37	85	72.8
		52	83.78			87	27.2
		53	9.43			88	0.56
		54	2.30			89	9.86
Mn	25	55	100	Sr	38	87	7.02
Fe	26	54	6.0			88	82.56
		56	91.6			89	100
		57	2.1	Y	39	90	48
		58	0.28			91	11.5
Co	27	57	0.2			92	22
		59	99.8	Zr	40	94	17
Ni	28	58	67.4			96	1.5
		60	26.7	Nb	41	93	100
		61	1.2			94	14.9
		62	3.8			95	9.40
		64	0.88	Mo	42	96	16.1
		65	68			97	16.6
Cu	29	63	32			98	9.65
Zn	30	64	50.9			99	24.1
		66	27.3	Ru	44	100	9.25
		67	3.9			96	5
		68	17.4			(98)	12
		70	0.5			99	14
Ga	31	69	61.2			100	22
Ge	32	71	38.8			101	30
		70	21.2	Rh	45	102	17
		72	27.3			104	0.1
		73	7.9			101	99.9
		74	37.1	Pd	46	103	0.8
		76	6.5			104	9.3
As	33	75	100			105	22.6
Se	34	74	0.9			106	27.2
		76	9.5	Ag	47	108	26.8
		77	8.3			110	13.5
		78	24.0			107	52.5
		80	48.0			109	47.5
		82	9.3	Cd	48	106	1.4
Br	35	79	50.6			108	1.0
Kr	36	81	49.4			110	12.8
		78	0.35			111	13.0
		80	2.01			112	24.2
		82	11.53			113	12.3
		83	11.53			114	28.0
		84	57.11			116	7.3
		86	17.47				

## APPENDIX I

Symbol	Atomic Number (Z)	Mass Number (A)	Relative Abundance (%)	Symbol	Atomic Number (Z)	Mass Number (A)	Relative Abundance (%)
In	49	113	4.5	Nd	60	142	25.95
		115	95.5			143	13.0
Sn	50	112	1.1	Sm	62	144	22.6
		114	0.8			145	9.2
		115	0.4			146	16.5
		116	15.5			148	6.8
		117	9.1			150	5.95
		118	22.5			144	3
		119	9.8			147	17
		120	28.5			148	14
		122	5.5			149	15
		124	6.8			150	5
Sb	51	121	56	Eu	63	152	26
		123	44			154	20
Te	52	120	w	Gd	64	151	49.1
		122	2.9			153	50.9
		123	1.6			152	0.2
		124	4.5			154	1.5
		125	6.0			155	21
		126	19.0			156	22
		128	32.8			157	17
		130	33.1			158	22
		127	100			160	16
		124	0.094	Tb	65	159	100
Xe	54	126	0.088			158	0.1
		128	1.90			160	1.5
		129	26.23			161	22
		130	4.07			162	24
		131	21.17			163	24
		132	26.96			164	28
		134	10.54			165	100
		136	8.95			166	0.25
		133	100			164	2
		130	0.101			167	35
Cs	55	132	0.097			168	24
		134	2.42			170	29
		135	6.6			170	10
		136	7.8			171	11.3
		137	11.3			172	71.7
		138	71.7	Tm	69	173	23
		139	100			174	17
La	57	w	Yb	70	168	175	0.06
		138	w			170	2
		140	89			171	9
		142	11			172	23
Ce	58	141	100			173	17
		142	37			174	37
Pr	59	141	100			176	12

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Symbol	Atomic Number (Z)	Mass Number (A)	Relative Abundance (%)	Symbol	Atomic Number (Z)	Mass Number (A)	Relative Abundance (%)
Lu	71	175	97.5	Pt	78	192	0.8
		176	2.5			194	30.2
Hf	72	174	0.3			195	35.3
		176	5			196	26.6
		177	19			198	7.2
		178	28			Au	100
		179	18			Hg	0.15
		180	30			196	10.11
		181	100			198	17.03
Ta	73	180	0.2	W	74	199	23.26
		182	22.6			200	13.17
		183	17.3			201	29.56
		184	30.1			202	6.72
		186	29.8			204	
Re	75	185	38.2	Tl	81	203	29.1
		187	61.8			205	70.9
Os	76	184	0.018			Pb	1.5
		186	1.58			204	23.5
		187	1.64			206	22.7
		188	13.3			207	52.3
		189	16.2			208	
		190	26.4	Bi	83	209	100
		192	40.9			Th	(100)
Ir	77	191	38.5			U	0.006
		193	61.5			234	0.71
						235	99.28

## APPENDIX II

### THE PERIODIC TABLE OF THE ELEMENTS

The atomic numbers are given in bold type, the atomic weights (International values for 1941) in italics and the isotopes in ordinary numerals. The roman numerals indicate the chemical groups and the most important associated valencies are given below them. Elements are placed to the left or to the right of the columns according to their chemical properties, those in the same vertical line as each other have strong chemical similarities. The Rare Earth

#### PERIODIC TABLE

<b>1 H</b>				
<i>1.0080</i>				
<i>1, 2</i>				
Valencies 0				
<b>2 He</b>	<b>3 Li</b>	<b>4 Be</b>	<b>5 B</b>	<b>6 C</b>
<i>4.003</i>	<i>6.940</i>	<i>9.02</i>	<i>10.82</i>	<i>12.010</i>
<i>3, 4</i>	<i>6, 7</i>	<i>9</i>	<i>10, 11</i>	<i>12, 13</i>
<b>10 Ne</b>	<b>11 Na</b>	<b>12 Mg</b>	<b>13 Al</b>	<b>14 Si</b>
<i>20.183</i>	<i>22.997</i>	<i>24.32</i>	<i>26.97</i>	<i>28.06</i>
<i>20, 21, 22</i>	<i>23</i>	<i>24, 25, 26</i>	<i>27</i>	<i>28, 29, 30</i>
<b>18 A</b>	<b>19 K'</b>	<b>20 Ca</b>	<b>22 Ti</b>	
<i>39.944</i>	<i>39.096</i>	<i>40.08</i>	<i>47.90</i>	
<i>36, 38, 40</i>	<i>39, 40, 41</i>	<i>40, 42, 43</i>	<i>46, 47, 48, 49</i>	
		<i>44, 46, 48</i>	<i>50</i>	
	<b>29 Cu</b>	<b>30 Zn</b>	<b>31 Ge</b>	<b>32 Ge</b>
	<i>63.57</i>	<i>65.38</i>	<i>69.72</i>	<i>72.60</i>
	<i>63, 65</i>	<i>64, 66, 67, 68, 70</i>	<i>69, 71</i>	<i>70, 72, 73, 74, 76</i>
<b>36 Kr</b>	<b>37 Rb</b>	<b>38 Sr</b>	<b>43 Zr</b>	
<i>83.7</i>	<i>85.48</i>	<i>87.63</i>	<i>91.22</i>	
<i>78, 80, 82, 83, 84,</i>	<i>85, 87</i>	<i>86, 88, 87, 88</i>	<i>90, 91, 92</i>	
<i>86</i>			<i>94, 96</i>	
	<b>47 Ag</b>	<b>48 Cd</b>	<b>49 In</b>	<b>50 Sn</b>
	<i>107.880</i>	<i>112.41</i>	<i>114.76</i>	<i>118.70</i>
	<i>107, 109</i>	<i>106, 108, 110, 111,</i>	<i>113, 115</i>	<i>112, 114, 115, 116,</i>
		<i>112, 113, 114, 116</i>		<i>117, 118, 119, 120,</i>
				<i>122, 124</i>
<b>54 Xe</b>	<b>55 Cs</b>	<b>56 Ba</b>	<b>57 La</b>	
<i>131.3</i>	<i>132.91</i>	<i>137.36</i>	<i>138.92</i>	
<i>124, 126, 128, 129,</i>	<i>133</i>	<i>130, 132, 134, 135,</i>	<i>139</i>	
<i>130, 131, 132,</i>		<i>136, 137, 138</i>		
<i>134, 136</i>				
<b>58 Ce</b>	<b>59 Pr</b>	<b>60 Nd</b>	<b>61—</b>	<b>62 Sm</b>
<i>140.13</i>	<i>140.92</i>	<i>144.27</i>		<i>150.43</i>
<i>136, 138, 140</i>	<i>141</i>	<i>142, 143, 144,</i>		<i>144, 147, 148,</i>
<i>142</i>		<i>145, 146, 148,</i>		<i>149, 150, 152,</i>
		<i>150</i>		<i>154</i>
<b>63 Eu</b>	<b>64 Gd</b>	<b>65 Tb</b>	<b>66 Dy</b>	<b>67 Ho</b>
<i>152.0</i>	<i>156.9</i>	<i>159.2</i>	<i>162.46</i>	<i>164.94</i>
<i>151, 153</i>	<i>152, 154, 155,</i>	<i>159</i>	<i>158, 160, 161</i>	<i>165</i>
	<i>156, 157, 158,</i>		<i>162, 163, 164</i>	
	<i>160</i>			
<b>68 Er</b>	<b>69 Tm</b>	<b>70 Yb</b>	<b>71 Lu</b>	<b>72 Hf</b>
<i>167.2</i>	<i>169.4</i>	<i>173.04</i>	<i>174.99</i>	<i>178.6</i>
<i>162, 164, 166,</i>	<i>169</i>	<i>168, 170, 171, 172,</i>	<i>175, 176</i>	<i>174, 176, 177, 178,</i>
<i>167, 168, 170</i>		<i>173, 174, 176</i>		<i>179, 180</i>
	<b>79 Au</b>	<b>80 Hg</b>	<b>81 Tl</b>	<b>82 Pb</b>
	<i>197.2</i>	<i>200.61</i>	<i>204.39</i>	<i>207.2</i>
	<i>197</i>	<i>196, 198, 199, 200,</i>	<i>203, 205</i>	<i>204, 206, 207, 208</i>
		<i>201, 202, 204</i>		
<b>86 Rn</b>	<b>87—</b>	<b>88 Ra</b>	<b>89 Ac</b>	<b>90 Th</b>
<i>222</i>		<i>226.05</i>		<i>232.12</i>
				<i>232</i>

## APPENDIX II

group is surrounded by a thick line. The properties of the missing elements can be predicted with considerable certainty from the positions of their atomic numbers. From the point of view of the construction of the atom the inert gases should mark the end of the periods ; on the other hand, it is more usual in chemistry to start with valency 0. From principles of general convenience of arrangement the latter plan is adopted in this table, which is intended to give the maximum amount of chemical information. Hydrogen, which belongs equally well to group I or group VII, is best omitted from the table altogether.

### OF THE ELEMENTS

V - 3	VI - 2	VII	VIII
		7 F	
7 <i>14-008</i> 14, 15	8 O <i>16-000</i> 16, 17, 18	19-00 19	
	16 S <i>32-06</i> 31      32, 33, 34, 36	17 Cl <i>35-457</i> 35, 37	
23 V <i>50-95</i> 51	24 Cr <i>52-01</i> 50, 52, 53, 54	25 Mn <i>54-93</i> 55	26 Fe <i>55-85</i> 54, 56, 57
	33 As <i>74-91</i> 75      74, 76, 77, 78, 80, 82	34 Se <i>78-96</i>	27 Co <i>58-94</i> 57, 59
41 Nb <i>92-91</i> 93	42 Mo <i>95-95</i> 92, 94, 95, 96, 97, 98, 100	43—	28 Ni <i>58-69</i> 58, 60, 61, 62, 64
			44 Ru <i>101-7</i> 96, 98, 99, 100, 101, 102, 104
51 Sb <i>121-76</i> 121, 123	52 Te <i>127-81</i> 120, 122, 123, 124, 125, 126, 128, 130	53 I <i>126-92</i> 127	45 Rh <i>102-91</i> 101, 103
73 Ta <i>180-88</i> 181	74 W <i>183-92</i> 180, 182, 183, 184, 186	75 Re <i>186-37</i> 185, 187	46 Pd <i>106-7</i> 102, 104, 105, 106, 108, 110
			47 Os <i>190-2</i> 184, 186, 187, 188, 189, 190, 192
83 Bi <i>209-00</i> 209	84 Po	85—	77 Ir <i>193-1</i> 191, 193
91 Pa <i>231</i>	92 U <i>238-07</i> 234, 235, 238		78 Pt <i>195-23</i> 192, 194, 195 196, 198

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